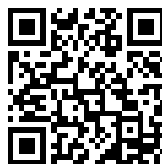

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THE METALLURGY OF HAFNIUM

Edited by
D. E. THOMAS
E. T. HAYES



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FOREWORD

This is the third book that has been published on the metallurgy of reactor materials under the sponsorship of the Naval Reactors group of the U.S. Atomic Energy Commission. The other two books are the *Metallurgy of Zirconium* and *The Metal Beryllium*, both of which were published in 1955. The nine books already published and six others presently under preparation, all sponsored by Naval Reactors, make up a comprehensive collation of some of the significant aspects of basic reactor technology which has been developed in the Naval Reactors program and the Shippingport Pressurized Water Reactor.

From its very inception, the Naval Reactors program has given great emphasis to development work on the metallurgy of reactor materials—fuel materials, control materials and structural materials. While this metallurgical development work has been guided largely towards pressurized water and sodium-cooled reactor applications, I believe that the basic understanding that has been obtained on the properties and fabricability of these materials is such that it will be of significant value to other industrial applications, both nuclear and non-nuclear.

Hafnium was discovered in 1922 and its name was taken from Hafnia, the Latin name of Copenhagen, where G. de Hevesy discovered hafnium. The technological development of hafnium has been closely connected with that of zirconium. Hafnium is normally found in nature with zirconium and, because of its strong tendency to absorb neutrons, must be removed from the zirconium before the zirconium can be used in nuclear reactors. Until 1951, the hafnium obtained from the hafnium-zirconium separation process was stored without any specific application in view at the time.

It was 1951 when the urgent need occurred for obtaining a reliable control material for the *Nautilus* land prototype reactor at Arco, Idaho, that such a specific application developed for hafnium. Since then, hafnium has been used for the control material of naval water-cooled reactors and for the Shippingport reactor. Its physical and nuclear characteristics have been found to be outstanding for this application; as a result hafnium now plays an important role among materials for water-cooled power reactors.

This book presents the technology developed to date on hafnium by the Naval Reactors program and the Shippingport Pressurized

Water Reactor. Much has been learned but much remains to be done especially in the field of hafnium alloys and compounds. I trust that metallurgists in industry will take up this challenge and continue further development.

I would like to extend my appreciation to the many persons who have given their time to the preparation of this book and to Dr. D. E. Thomas and Dr. E. T. Hayes for their efforts in editing it.

H. G. RICKOVER,
Vice Admiral, USN.

EDITORS' PREFACE

The past decade or so has seen the rapid development of the trio of Group IV transition metals, titanium, zirconium, and hafnium, from the laboratory curiosity stage to the production stage. Because of the unusual similarity in their chemical properties, zirconium and hafnium always occur together in nature. In their respective abilities to absorb neutrons however they differ greatly, and this difference has led to their use in nuclear reactors. Zirconium, with a low neutron absorption cross section (0.18 barns), is highly desirable as a structural material in water-cooled nuclear reactor cores. Hafnium, on the other hand, because of its high neutron absorption cross section (105 barns) can be used as a neutron absorbing control material in the same nuclear reactor cores. Thus, these two elements which occur together so intimately in nature that they are very difficult to separate are used together as separate important components in the cores of nuclear reactor plants.

The technological development of hafnium stems in large measure from the impetus and direction afforded by Vice Admiral H. G. Rickover, Assistant Director, Division of Reactor Development, Atomic Energy Commission, and Assistant Chief for Nuclear Propulsion, Bureau of Ships. His decision in May 1950 to utilize zirconium in the *Nautilus* reactor and its land-based prototype required among other things that a process for the large scale separation of hafnium from zirconium be developed and placed on a production basis. Hafnium was a byproduct of the production of zirconium. As there was no specific use for it at that time the hafnium was put in storage. A subsequent decision by Vice Admiral Rickover in 1951 to use hafnium for the control rod material in the same reactors was the beginning of the exploitation of this new metal—hafnium. Since that time hafnium has been employed in a wide variety of water-cooled reactors including most of the naval reactors and the Shippingport Pressurized Water Reactor.

A considerable amount of work has been performed since 1951 as a result of the application of hafnium as a control rod material. The nuclear physics aspects involved in using hafnium in reactors have been worked out in detail. Metallurgical work, particularly long-time corrosion tests in high temperature water, has been performed and has shown that hafnium is satisfactory for this application. Means of melting, forging, rolling, and welding hafnium into precision components have been developed.

It has been fortunate for the development and procurement of satisfactory nuclear reactor control rods that no major problems have arisen with hafnium which could not be solved by leaning heavily on the vast technology developed concurrently for zirconium. However, this lack of major problems has, in itself, resulted in some significant technical areas remaining unexplored. For example, unalloyed hafnium may be used in the control rods for water-cooled reactors since its properties are adequate for the application; consequently a large-scale alloy development program has not been necessary. This is just one indication of the fact that much remains to be done in the field of hafnium metallurgy.

This book is based largely on the development and fabrication work that was performed on hafnium to permit its use in water-cooled reactor cores. Much of the knowledge that was obtained in this connection resides in unpublished letters and reports or in documents not generally available. The purpose of this book is, therefore, to assemble and critically review this information and thereby facilitate its dissemination. It is hoped that this will interest workers in industrial and research activities to contribute to the further development of hafnium technology.

The editors wish to express their thanks to Vice Admiral Rickover, without whose support and encouragement this book would not have been possible; to the chapter editors and section authors for their contributions; to the management of their respective organizations for support in the preparation of the book; and finally, to the many people who have reviewed portions of the manuscript and assisted in its preparation.

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Chapter 1

APPLICATION OF HAFNIUM

W. H. WILSON,¹ *Editor*

This chapter is divided into four parts. First, the history of the discovery, the development, and the application of hafnium is discussed. Second, the nuclear properties of hafnium are covered, since the principal application has been as the metal of construction in control rods for nuclear reactors. The third and fourth sections cover the nuclear and nonnuclear uses of hafnium.

1.1 HISTORY OF HAFNIUM

By W. H. Wilson and R. W. Staehle¹

Introduction

The recent history of hafnium begins with the decision in 1950 to manufacture hafnium-free zirconium metal for use in the reactor core of the submarine *Nautilus*. The next year, it was decided to use the byproduct hafnium in the neutron absorbing control rods in the same reactor. The first core using hafnium control rods was the *Nautilus* prototype reactor plant at the Naval Reactor Test Site in Arco, Idaho. This reactor went to power on May 31, 1953. The second core also employing hafnium control rods was used in the *Nautilus* and propelled that ship for 60,000 miles. The satisfactory performance of hafnium control rods has resulted in the use of hafnium in a wide variety of water-cooled reactors including the Shippingport pressurized water reactor.

Since hafnium was not discovered until 1922, its history is short compared with that of most other elements. Although zirconium was discovered in 1789 by Klaproth, and elemental metallic zirconium was made by Berzelius in 1824, there is no indication that these early investigators suspected that there was about 2 percent hafnium in their zirconium. However, in view of the chemical similarity of zirconium and hafnium and the lack of X-ray analytical techniques, it is not surprising that hafnium went undetected by these early investigators.

¹ Naval Reactors, USAEC, Washington, D.C.

In France in 1911, George Urbain [1] announced the discovery of a new element which he erroneously thought was element number 72. Urbain's claim, which was never widely accepted, touched off a round of claims and counter-claims and the matter was not finally settled for some time.

Between 1911 and 1922, it was deduced that element 72 was similar to titanium and zirconium and that it might be expected to occur with zirconium ores. George de Hevesy (von Hevesy) is credited with discovering hafnium in 1922.

Early History of Hafnium

In 1911, Urbain presented evidence to indicate that a material he had separated from rare earth ores was a new element, and he called the new element "celtium." Since this new material had properties intermediate between lutetium and yttrium, Urbain suggested that celtium was a rare earth. In 1922, after a long period of military duties, Urbain resumed his search for element 72 using X-ray techniques. At Urbain's suggestion, in 1922, A. Dauvillier [2] using an improved X-ray technique, observed two faint lines in Urbain's original material. Dauvillier announced that the material (Urbain's original material) contained element number 72 and that these new X-ray lines could be assigned to no other element.

Hafnium and the Periodic Table

In the latter half of the 19th century, Dmitri Mendeleev presented to the Russian Chemical Society his famous paper on "The Relation of the Properties to the Atomic Weights of the Elements." In Mendeleev's periodic table, titanium, zirconium, cerium, and thorium were presented as homologous elements in Group IV. A serious search for hafnium does not appear to have been prompted since cerium (which can have a valence of four as does zirconium) was listed in Group IV following zirconium. From a modern standpoint, Mendeleev's periodic table was confused because atomic weights instead of atomic numbers were used for classification and because the role of the rare earths was not understood.

A second significant contribution to understanding the periodicity of the elements was the arrangement of the elements by electronic structure. Julius Thomson, in 1895, presented the first outline of electronic structure. This concept of periodic structure was clarified by Neils Bohr in 1922 [3]. In this arrangement of the atoms on the basis of electronic structure, it was unmistakably clear that there should be an element number 72 which had not yet been discovered.

A discovery which greatly facilitated the actual identification of element 72 was made by Henry Moseley, who determined, about

1910, that the atomic number is inversely proportional to the square root of the wavelength of a given line-group in the X-ray spectra emitted from the various elements. At that time, elements 43, 61, 72, 75, 85, 87, and 91 in the periodic table were undiscovered. Element 72 (hafnium) was the first of the elements to be discovered using Moseley's X-ray relationship.

De Hevesy's Discovery

At the suggestion by Bohr that element 72 should be found in quadrivalent zirconium rather than in the generally tetravalent rare earths, Dirk Coster and George de Hevesy looked in zirconium ores for the new element. In January 1923, they announced² that they had discovered element number 72 and named it "hafnium" in honor of Copenhagen (Latin "Hafnia" is the word for Copenhagen). The element number 72 was named for Copenhagen because Coster and de Hevesy were associated at the time with the Institute of Theoretical Physics in Copenhagen. (It is interesting to note that neither Professor Coster nor Professor de Hevesy was Danish. Coster was from the Netherlands and de Hevesy was from Hungary.)

Coster and de Hevesy's first paper [4] identified six prominent X-ray lines that conformed exactly to theoretical predictions made on the basis of Bohr's and Thompson's electronic theory. In the same paper they stated that the material observed by Urbain and Dauvillier could not have been element number 72 since the wavelength of the X-ray lines differed by more than experimental error from theoretical predictions and from the lines that Coster and de Hevesy had actually observed on their zirconium sample. Coster and de Hevesy also indicated that the two extremely faint X-ray lines which were observed by Dauvillier provided only a questionable indication of the presence of hafnium.

Following the claim by Coster and de Hevesy for discovery of hafnium as element number 72, a vigorous debate lasted for almost two years. Urbain and Dauvillier checked the spectra obtained from their gadolinite with those obtained from a zirconium sample containing hafnium and asserted that the lines were identical. Dauvillier also claimed that his techniques had greater sensitivity than did those of Coster and de Hevesy. In 1923, Dauvillier admitted that his earlier values differed from theoretical predictions, but held that the difference was within experimental error and that redetermination of the lines brought his original values closer to theoretical. In response to the objection that it would be extremely unlikely for hafnium to accompany rare earths in the mineral form, Urbain

² This article appeared in January 1923 while the actual discovery occurred in 1922. Consequently, the date for discovery of hafnium is taken as 1922.

pointed to analyses which showed that ytterbium, zirconium, and hafnium were found as major constituents in the minerals alvite and malacon. No data were reported, however, which indicated that zirconium occurred with any rare earth other than ytterbium.³

The additional evidence of Urbain and Dauvillier was strongly disputed by Coster and de Hevesy and their supporters. Werner and Hansen [5] showed that the spectral lines observed by Urbain in 1911 coincided not with those of hafnium but with those of lutetium observed by Eder in 1915. Werner and Hansen also observed that none of Urbain's spectral lines occurred in the spectrum of specimens containing 90 percent hafnium. It is significant that Moseley and Urbain had also examined rare earth residues supposedly containing the new element and could find X-ray lines attributable only to ytterbium (number 70) and lutetium (number 71) and not to element 72. It was also noted that, upon re-examination of optical spectra of zirconium back to 1910, hafnium lines were present as weak lines in the zirconium spectrum.

In 1924, the Fourth Report of the German Atomic Weight Commission announced "hafnium" to be the preferred name of element number 72 with Coster and de Hevesy as discoverers. This pronouncement appeared to have settled the issue, and thereafter "hafnium" was the name given preference by all scientists except those in France. The name "celtium" appears to have been used by French scientists until 1949. In 1949, at the 15th Conference of the International Union of Pure and Applied Chemistry, an attempt was made to settle the names of controversial elements and "hafnium" was recommended as the name for element 72.⁴ Apparently French scientists have accepted this name. The periodic table in *Techniques de L'Ingenieur* (Editor C. Monteil) traditionally used celtium for element 72, but in 1952, this handbook showed hafnium in the position of element 72.

Early Work on Hafnium

Concurrent with the discovery of hafnium, attention was given to the question of how much hafnium could be expected to occur with zirconium. Between 1923 and 1928, ores were reported with hafnium contents varying from 0.17 percent (in a Brazilian mineral) to 60 percent (reported in thortveitite) of the combined zirconium and hafnium assay. These ratios are extremes, and de Hevesy observed that most zirconium ores showed a hafnium-zirconium content of

³ The mineral beckelite contains Y, Ce, La, Nd, Pr, Zr, and Hf.

⁴ At the same conference, the name niobium was accepted over columbium for element number 41, beryllium over glucinium for element 4, and wolfram over tungsten for element number 74. In addition, the official names for elements 93-96 were accepted as neptunium for 93, plutonium for 94, americium for 95, and curium for 96.

2 to 3 percent. It is interesting to note that several investigations in the latter half of the 19th century suspected the presence of a heavier unknown element in zirconium ores, but none of these claims was ever substantiated. This confusion probably resulted from the fact that both uranium and thorium sometimes occur with zirconium ores [6].

The first articles on the isotopic content of hafnium were published in 1935. Other articles followed, and by 1944 [7] the values were in substantial agreement with those being used today. De Hevesy and Levi first noted that neutron bombardment produced radioactivity in hafnium and suggested a half life of 55 ± 7 days for hafnium 181 (compared with the 46-day half life which is the currently accepted value).

An observation was made by Lee in 1928 [8] that ores containing zirconium and hafnium were generally radioactive in proportion to the amount of hafnium present. He suggested that this resulted from the presence of uranium and thorium which he considered to be isomorphous with hafnium.

The first "hafnium free" zirconium was produced by Coster and de Hevesy in 1923. The hafnium content was reduced until it could not be observed in the zirconium by X-ray techniques. As a by-product of this technique a Hf-50 percent Zr material was produced. De Hevesy and Jantzen, in 1923, produced a sample of hafnium metal containing 99 percent hafnium. The work on separating the two materials was pursued enthusiastically for the next 10 years with a large number of patents being obtained for separation techniques. Principal methods for separation were fractional crystallization techniques using sulphates, halogen compounds, complex oxalates, sodium hydroxide, and phosphates. A survey of separation techniques is given in Chapter 2.

Methods of purifying hafnium and producing ductile metal were first published in 1925. De Boer and van Arkel suggested that hafnium could be produced by the thermal decomposition of hafnium iodide on a heated filament (crystal bar process). In 1925, a patent was obtained for producing hafnium by this process. In 1930, de Boer and Fast converted hafnium dioxide to metal by calcium, magnesium, and sodium reductions and subsequently used the crystal bar process to obtain ductile hafnium.

Early determinations of the atomic weight were hampered by the presence of zirconium, and the first estimate, published in 1923, was 180. This value was obtained by extrapolation using a sample containing 6 percent Zr. In 1927, the weight of 178.6 was agreed upon by the Committee on Atomic Weights. The internationally accepted value today is 178.5.

Recent History of Hafnium

Hafnium is obtained from zirconium ores. In general, the percentage of hafnium in zirconium ores is about 2 percent by weight. The use of zirconium as a structural material in nuclear reactors required practically complete elimination of hafnium in order to realize the low neutron absorption cross section (0.18 barns) of hafnium-free zirconium.⁵ Although a goal of reducing the hafnium content to 0.1 percent was established, the best methods were tedious and would not reduce hafnium levels below 0.5 percent without difficulty. Research work was expanded to meet the challenge, and, in 1949, over ten organizations were working on zirconium-hafnium separation methods. One method has proved to be excellent—extraction of hafnium salts from an aqueous liquid into an organic liquid—hexone. In 1950, this liquid-liquid extraction process was set up at the Y-12 site, Oak Ridge, Tenn., to remove hafnium from zirconium. Despite difficulties with equipment, the process proved capable of producing zirconium with less than 0.01 percent hafnium. The process was classified and remained so for over 5 years, which prevented its disclosure in the open literature. A complete description of this process and others is presented in Chapter 2. In addition to separation studies, some work was undertaken at Oak Ridge to make pound quantities of ductile hafnium metal using calcium reduction in a small steel vessel or “bomb.”

In October 1950, A. Radkowsky, of the Naval Reactors group, calculated that the high resonance neutron capture cross section would enhance the value of hafnium as a control rod material. These studies were confirmed at Argonne National Laboratory by experimental comparison of the control worth of a small piece of metallic hafnium with a corresponding piece of silver-cadmium alloy. In 1951, when it was decided to use the discarded byproduct hafnium hydroxide from the Oak Ridge separation process to make the control rods for the prototype of the *Nautilus* reactor core, emphasis was placed on the production of hafnium as well as zirconium metal.

The first step in obtaining large amounts of hafnium was the adjustment of the liquid-liquid separation process to produce a higher hafnium-to-zirconium ratio in the side stream (the main stream was zirconium with about 0.01 percent hafnium). The side

⁵ It is interesting to note that prior to 1947, the thermal neutron absorption cross section of zirconium was thought to be about 2.5 barns [9]. In 1948, workers at Oak Ridge National Laboratory reported a zirconium cross section of 0.4 barns and established that the discrepancy was due to the presence of hafnium which has a cross section of 105 barns for thermal neutrons. Later, when purer zirconium was available, the cross section was measured to be 0.18 ± 0.02 barns [10].

stream was adjusted so that the metal content was about 95 percent hafnium, the major metallic impurities being zirconium, titanium, and iron.

The hafnium oxide resulting from the liquid-liquid extraction process was reduced with magnesium at the Bureau of Mines station at Albany, Oreg. Magnesium reduction (called the Kroll process in honor of William J. Kroll), which was being used exclusively for production of zirconium sponge, was found to work well with hafnium. Because of the oxygen and other impurities in the Kroll sponge hafnium, it was necessary to refine it further by the crystal bar process (as was also necessary for zirconium sponge in 1951). The resulting crystal bar hafnium metal is easily melted and worked by processes established for zirconium.

The production of hafnium and zirconium since 1948 is presented in Table 1.1. It can be seen that production of hafnium metal rose from 3,100 pounds in 1952 to about 20,000 pounds in 1958, and the price of hafnium has decreased steadily as production increased. There are several reasons why the production of hafnium shown in Table 1.1 is considerably less than the amount which is available (1.8 percent) in the zirconium ores now used. First, the losses in the crystal bar process materially reduce the quantity of hafnium produced, whereas these losses do not occur in the direct melting process used in zirconium production. Furthermore, the processing time is longer. When production is expanding this factor is important since hafnium production would tend to be limited by the previous year's zirconium production.

In the case of zirconium, it was possible to eliminate the need for the iodide process. At this writing, the iodide process is still being utilized in the production of hafnium. However, it appears that improvements in the Kroll process and subsequent melting in high vacuum may supplant the iodide process in the near future.

As can be seen from the above, the development of hafnium has paralleled that of zirconium because of the similarities of their properties and their applications. A complete account of the work done on development of zirconium and a description of its properties are recorded in the *Metallurgy of Zirconium* [9]. No attempt has been made in this book on hafnium to duplicate any of the material in that reference.

TABLE 1.1—PRODUCTION OF ZIRCONIUM AND HAFNIUM

| Calendar year | Pounds of reactor grade zirconium | Price per pound of zirconium | Pounds of hafnium crystal bar | Price per pound of hafnium crystal bar |
|---------------|-----------------------------------|------------------------------|-------------------------------|--|
| 1948----- | 1, 000 | \$300 | ----- | ----- |
| 1949----- | 3, 000 | 150 | ----- | ----- |
| 1950----- | 10, 000 | 110 | ----- | ----- |
| 1951----- | 29, 000 | 50 | ----- | ----- |
| 1952----- | 51, 000 | 40 | 3, 100 | \$93 |
| 1953----- | 200, 000 | 12 | 5, 000 | 70 |
| 1954----- | 310, 000 | 13 | 7, 800 | 53 |
| 1955----- | 330, 000 | 13 | 4, 900 | 46 |
| 1956----- | 475, 000 | 13 | 6, 900 | 57 |
| 1957----- | 1, 080, 000 | 11 | 12, 700 | 52 |
| 1958----- | 2, 000, 000 | 8 | 18, 100 | 40 |
| 1959----- | ¹ 2, 200, 000 | ¹ 7 | ¹ 25, 000 | ¹ 39 |

¹ Estimated.

1.2 NUCLEAR PROPERTIES OF HAFNIUM

By A. Radkowsky,⁶ D. N. Schmoker,⁶ and J. J. Sullivan⁶

Nuclear Cross Sections

Naturally occurring hafnium is composed of six stable isotopes and has a gram atomic weight of 178.5 grams. Natural hafnium has a microscopic thermal (0.0253 ev) neutron absorption cross section of 105 ± 5 barns and a scattering cross section of 8 ± 2 barns. Table 1.2

TABLE 1.2—STABLE HAFNIUM ISOTOPES
[11, 12, 13]

| Isotope | Percent Abundance | σ_a (0.0253 ev) Barns | Approximate Contribution in Barns to σ_a of Natural Hf |
|-------------------------|-------------------|------------------------------|---|
| Hf ¹⁷⁴ ----- | 0. 18 | 1500 \pm 1000 | 2. 7 |
| Hf ¹⁷⁶ ----- | 5. 15 | 15 \pm 15 | C. 8 |
| Hf ¹⁷⁷ ----- | 18. 39 | 380 \pm 30 | 69. 9 |
| Hf ¹⁷⁸ ----- | 27. 08 | 75 \pm 10 | 20. 3 |
| Hf ¹⁷⁹ ----- | 13. 78 | 65 \pm 15 | 9. 0 |
| Hf ¹⁸⁰ ----- | 35. 44 | 14 \pm 5 | 5. 0 |

⁶ Naval Reactors, USAEC, Washington, D.C.

gives the cross section of each stable isotope in natural hafnium and gives the approximate contribution of each isotope to the total absorption cross section of natural hafnium.

It can be seen that the isotopes Hf-177, Hf-178, and Hf-179 account for approximately 100 barns of the thermal neutron absorption cross section of natural hafnium.

Several unstable isotopes of hafnium exist. Table 1.3 lists those isotopes which have been identified. The absorption cross sections of these unstable isotopes are unknown.

TABLE 1.3—UNSTABLE HAFNIUM ISOTOPES [14, 15]

| Isotopes | Half Life | Mode and Energy of Decay |
|---------------------------------------|--------------|--|
| Hf ¹⁷⁰ ----- | 1.87 hr----- | 2.4 mev β . |
| Hf ¹⁷¹ ----- | 16 hr----- | k electron capture, 1.02 and 0.63 mev γ 's. |
| Hf ¹⁷² ----- | 5 yr----- | k electron capture, 0.28 and 0.08 mev γ 's. |
| Hf ¹⁷³ ----- | 23.6 hr----- | k electron capture, 0.3 and 0.12 mev γ 's. |
| Hf ¹⁷⁵ ----- | 70 d----- | k electron capture, 0.343 and 0.089 mev γ 's. |
| ¹ Hf ^{179*} ----- | 19 s----- | internal conversion, 0.16 and 0.22 mev γ 's. |
| ¹ Hf ^{180*} ----- | 5.5 hr----- | isomeric transition, 0.57 and 0.44 mev γ 's. |
| Hf ¹⁸¹ ----- | 46 d----- | 0.41 mev β ; 0.13 and 0.48 mev γ 's. |
| Hf ¹⁸³ ----- | 64 m----- | 1.4 mev β ; 1.75 mev γ 's. |

¹ Hf^{179*} and Hf^{180*} refer to isomeric states which decay to stable hafnium isotopes of the same mass. This permits the identification of these isotopes by activation analysis. The Hf¹⁸⁰ isotope is one of the few even-even nuclei that have a metastable state.

As can be seen in Figure 1.1 [11, 16, 17, 18] the resonance structure of hafnium is quite profuse. Seven resonance peaks of high cross section have been identified between 1.0 and 10 ev. When the cross section is considered to be a function of the logarithm of the energy, the resonances become more dense in the region 10 to 100 ev; however, the peak cross sections are only about 100 barns or less. The level parameters for resonances between 1.0 and 15 ev are listed in Table 1.4. In Table 1.4, Γ_γ and Γ_n are the level widths representing the probabilities of the emission of photons and neutrons respectively by the compound nucleus in a specific quantum state. $\Gamma_{n_0} = \Gamma_n/E_0$ is called the "reduced" neutron width.

TABLE 1.4—PRINCIPAL ABSORPTION RESONANCES [11, 19, 20]

| Energy (ev) | Isotope | Peak Absorption Cross Section (Barns) | Γ_γ (Millivolts) | Γ_a (Millivolts) | Γ_{Σ} (Millivolts) |
|-----------------------|-------------------|--|---------------------------------|----------------------------|-----------------------------------|
| 1.1 ± 0.002 ----- | Hf ¹⁷⁷ | 4, 950 | 67 ± 2 | 2.1 ± 0.5 | 2.0 ± 0.5 |
| 2.38 ± 0.01 ----- | Hf ¹⁷⁷ | 5, 800 | 60 ± 1 | 9.1 ± 0.2 | 5.90 ± 0.13 |
| 5.69 ± 0.05 ----- | Hf ¹⁷⁹ | 1, 400 | ----- | 4.2 ± 1.3 | 1.8 ± 0.6 |
| 5.9 ± 0.01 ----- | Hf ¹⁷⁷ | 1, 100 | ----- | 5.1 ± 1.5 | 2.1 ± 0.6 |
| 6.6 ± 0.1 ----- | Hf ¹⁷⁷ | 7, 200 | 44 ± 20 | 11 ± 3 | 4.3 ± 1.3 |
| 7.8 ± 0.1 ----- | Hf ¹⁷⁸ | 9, 700 | ----- | 49 ± 3 | 17.5 ± 1.0 |
| 8.8 ± 0.1 ----- | Hf ¹⁷⁷ | 7, 400 | ----- | 8 ± 3 | 2.7 ± 1.1 |
| 13.7 ± 0.2 ----- | Hf ¹⁷⁷ | 130 | ----- | 0.67 ± 0.08 | 0.18 ± 0.02 |

Hf-177, the large thermal absorber, possesses most of the resonance peaks including the first two thermal peaks. The odd-N isotopes (Hf-177 and Hf-179) have a smaller level separation than the even-N isotopes. Hf-177 has an average level separation of about 3 ev, and Hf-178 has an estimated level separation of about 100 ev. Resonance scattering levels have been identified at about 6.7 ev for Hf-177 and about 7.6 ev for Hf-178 [12]. As shown in Figure 1.2 [21, 22], the hafnium total cross section remains constant at about 7 barns in the range of 1 to 3 mev.

For quick nuclear calculations involving natural hafnium, the constants listed in Table 1.5 may be of help. It should be noted that the values given are at 25° C, and, if Table 1.5 is to be used for calculations at elevated temperatures, suitable adjustments must be made on the listed values.

TABLE 1.5—NUCLEAR PROPERTIES (25°C)

| | |
|---|------------------------|
| Atomic weight----- | 178.5 |
| Density, ρ ----- | 13.09 g/cc at 20°C |
| Nuclei/cc ($\times 10^{-24}$)----- | 0.044 |
| Average logarithmic energy decrement, ξ ----- | 0.0113 |
| Total cross section, σ_t (0.0253 ev)----- | 113 barns |
| Scattering cross section, σ_s (0.0253 ev)----- | 8 barns |
| Absorption cross section, σ_a (0.0253 ev)----- | 105 barns |
| Macroscopic total cross section, Σ_t (0.0253 ev)----- | 5.1 cm^{-1} |
| Macroscopic scattering cross section, Σ_s (0.0253 ev)----- | 0.36 cm^{-1} |
| Macroscopic absorption cross section, Σ_a (0.0253 ev)----- | 4.7 cm^{-1} |
| Mean free path (all reactions), λ_t ----- | 0.196 cm |
| Scattering mean free path, λ_s ----- | 2.78 cm |
| Absorption mean free path, λ_a ----- | 0.21 cm |
| Slowing down power, $N\sigma_s\xi$ ----- | 0.004 |
| Moderating ratio, $\frac{\sigma_s\xi}{\sigma_a}$ ----- | 0.001 |

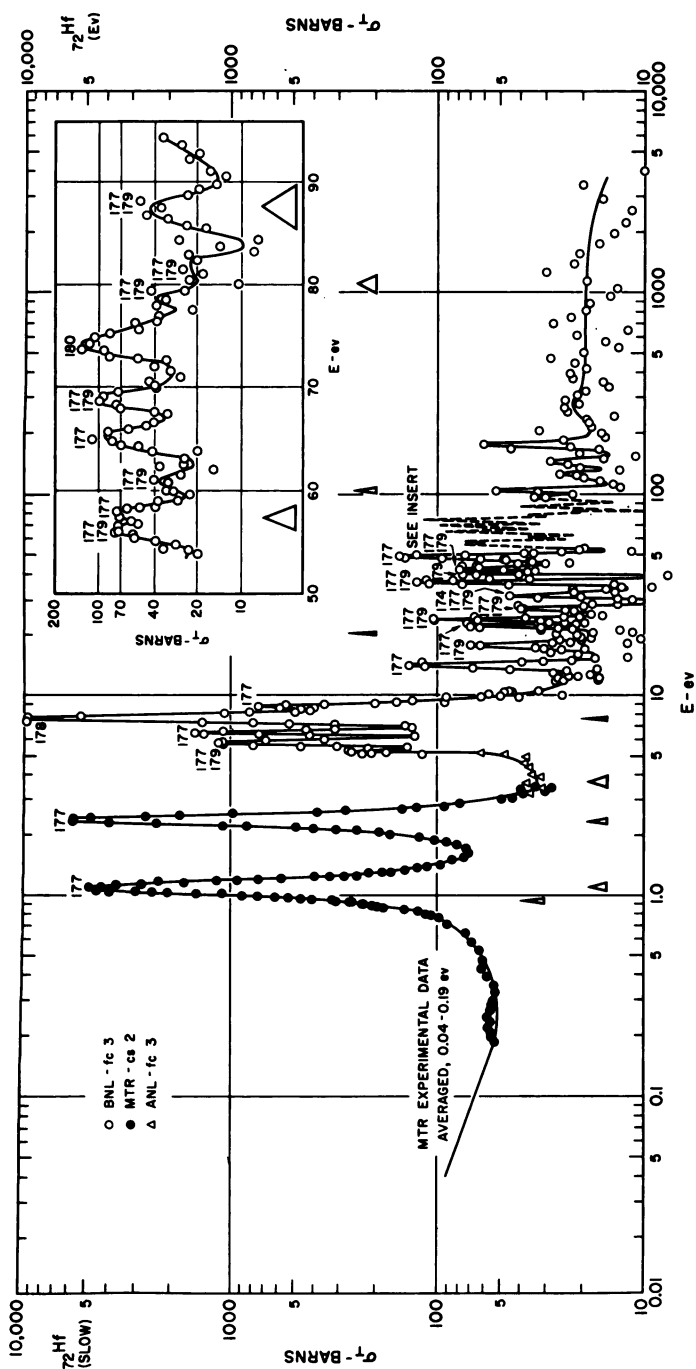


FIGURE 1.1. Hafnium Resonance Structure.

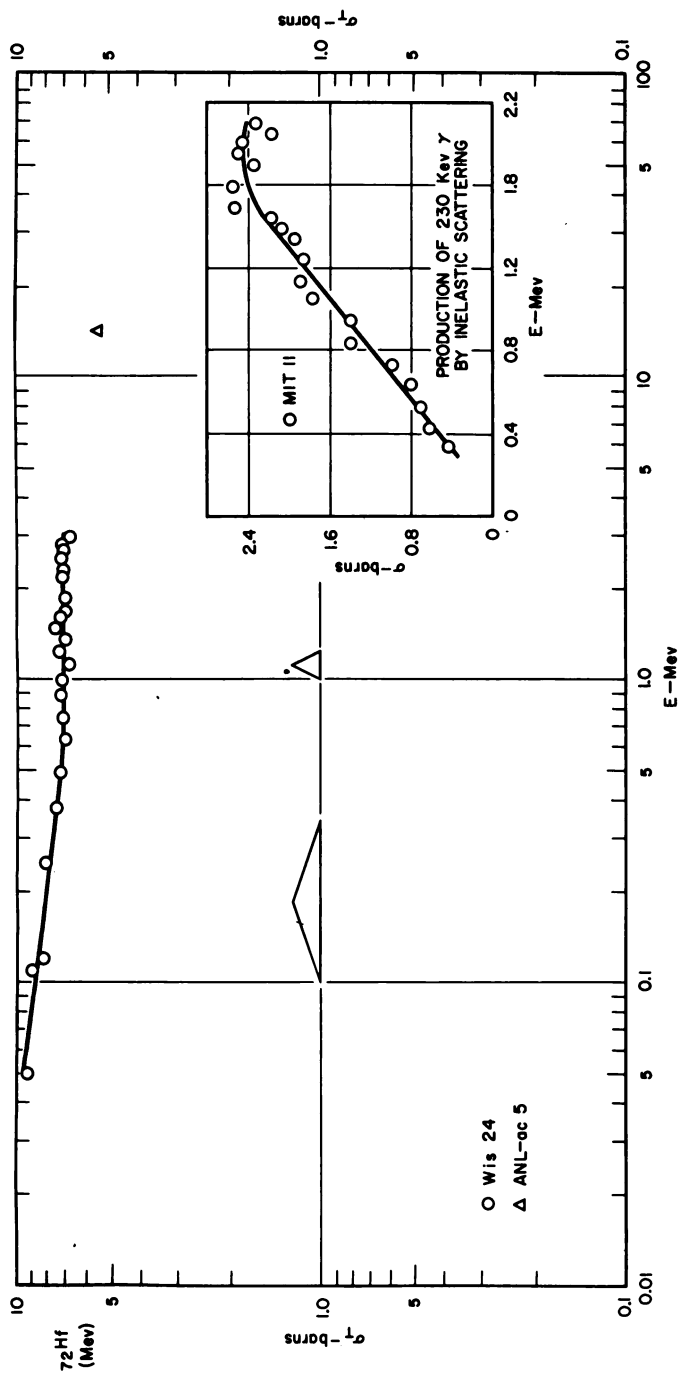
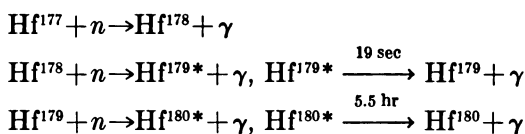


FIGURE 1.2. Hafnium Cross Section.

Nuclear Changes

Natural hafnium has an advantage over many other highly neutron absorbing elements, such as boron, in that its absorption cross section does not decrease markedly after long periods of irradiation. This is true since the existence of successive hafnium isotopes with large absorption cross sections permits the neutron absorption by one hafnium atom to result in the formation of a new hafnium isotope which also has a significant absorption cross section. The major cause of decreased absorption in irradiated hafnium is the burnup of the Hf-177 isotope which has the greatest thermal and resonance cross sections. The important transmutations occurring during hafnium irradiation are:



where Hf^{179*} refers to the excited state of Hf-179, and Hf^{180*} refers to the excited state of Hf-180. This production-destruction process is characterized by the following coupled differential-integral equations:

$$\begin{aligned}\frac{dN^{\text{Hf}^{177}}}{dt} &= - \int_j \int_E N^{\text{Hf}^{177}}(j) \sigma_a^{\text{Hf}^{177}}(E) \Phi(j, E) dj dE \\ \frac{dN^{\text{Hf}^{178}}}{dt} &= \frac{dN^{\text{Hf}^{177}}}{dt} - \int_j \int_E N^{\text{Hf}^{178}}(j) \sigma_a^{\text{Hf}^{178}}(E) \Phi(j, E) dj dE \\ \frac{dN^{\text{Hf}^{179}}}{dt} &= \frac{dN^{\text{Hf}^{178}}}{dt} - \int_j \int_E N^{\text{Hf}^{179}}(j) \sigma_a^{\text{Hf}^{179}}(E) \Phi(j, E) dj dE\end{aligned}$$

where

$j=x, y, z$ refers to the position coordinates in the reactor,

$N^{\text{Hf}^{177}}$ refers to the number of Hf-177 nuclei per cc etc.,

$\sigma^{\text{Hf}^{177}}(E)$ refers to the microscopic cross section of Hf-177 as a function of E , the incident neutron energy etc., and

$\Phi(j, E)$ is the energy- and space-dependent neutron flux.

If the spatial distribution and the energy spectrum of the neutron flux were known, and if the isotopic distribution of the hafnium were also known, the isotopic depletion and production could be computed for each spatial point. The resulting isotopic distribution could then be used to generate the succeeding distribution and so on to determine the burnup condition after a given amount of irradiation. General figures for burnup percentages cannot be given since

they depend on (a) flux distribution and spectrum, (b) the change in the hafnium absorption cross section with moderator temperature, and (c) the variation of the irradiation flux with time (in a reactor with constant power output the flux usually increases with lifetime due to fuel depletion).

The depletion data listed in Table 1.6⁷ apply to a reactor in which the average thermal flux throughout lifetime in a hafnium control rod is about 3×10^{13} n/cm²-sec.

TABLE 1.6—HAFNIUM DEPLETION AND TRANSMUTATION [23]

| Isotope | Fraction of isotope destroyed ¹ | | Fraction of isotope remaining ² (including production) | |
|-------------------------|--|------------------------|--|------------------------|
| | 5×10^{20} nvt | 5×10^{21} nvt | 5×10^{20} nvt | 5×10^{21} nvt |
| Hf ¹⁷⁷ ----- | 0. 087 | 0. 166 | 0. 913 | 0. 834 |
| Hf ¹⁷⁸ ----- | 0. 0157 | 0. 0314 | 1. 04 | 1. 08 |
| Hf ¹⁷⁹ ----- | 0. 0154 | 0. 0308 | 1. 01 | 1. 03 |
| Hf ¹⁸⁰ ----- | 0. 0023 | 0. 0046 | 1. 01 | 1. 01 |

¹ Ratio of the number of the particular isotope destroyed to the original number of the particular isotope.

² Ratio of remaining plus transmuted isotopes to the original number of the particular isotope.

After an nvt of 10^{21} (one year of continuous operation at the assumed flux), the a/o of each isotope present would be such that the rod would be worth about 95 percent of its original value.

Effectiveness of Hafnium as a Control Material

Although hafnium has been considered for use as a burnable poison and as a local flux suppressor, the principal use for hafnium in a reactor has been as a control rod material. The nuclear advantages of hafnium as a control rod material are (a) it does not decrease appreciably in worth upon irradiation, and (b) it absorbs both thermal and epithermal neutrons. Because of the appreciable resonance capture in hafnium, it has been found that its rod worth in a given core position does not decrease as much as an equivalent thermal absorber with an increase in core fuel loading (i.e., the spectrum shift to higher energies with increasing core blackness does not cause a large reduction in the effective hafnium cross section).

The control worth of a particular material at position x in the reactor depends on the product of the probability that a neutron

⁷ The data in Table 1.6 were calculated using the total absorption effectiveness (A).

of energy E and position x will be absorbed by the material and the importance function (i.e., the weight that a neutron of energy E and position x will have in reproducing the neutron population after a large number of succeeding generations). Some indication of the effectiveness of a control rod material may be obtained by determining the total absorption of neutrons of all energies. If it is assumed, as is approximately true in most cases, that the material is a $1/v$ absorber except at nonoverlapping resonances which follow the Breit-Wigner law, the absorptions fall into the following three classes:

- (1) the $1/v$ absorption of the thermal flux,
- (2) the $1/v$ absorption of the epithermal flux, and
- (3) the resonance absorption of the epithermal flux.

If we assume the material is in a thermal flux which has a Maxwellian distribution for the thermal region which extends up to E_1 and a $1/E$ epithermal energy distribution above E_1 , it can be shown, for a slab geometry [23, 24], that the total absorption, A , can be given as:

$$A = 1/2 F_1(y) + C F_2(x) + \frac{2C\sqrt{\pi}\sqrt{Nt}}{3} \sum_i \frac{\sqrt{c_i \sigma_{oi}} \Gamma \gamma_i}{E_0} \quad (1)$$

where the first, second, and third terms correspond to the above absorption classes a, b, and c, respectively,

$$y = Nt\sigma_{th}$$

$$x = Nt\sigma(E_1),$$

t = the thickness of the control rod slab (cm),

c_i = fractional abundance of the isotope with the resonance cross section,

σ_{oi} = absorption cross section at the resonance peak,

$\Gamma \gamma_i$ = capture width of the i^{th} resonance, and

$F_1(y)$ and $F_2(x)$ are complicated functions of y and x , respectively (see Tables 1.7 and 1.8 for characteristic values).

C is a constant which is related to the ratio of the average thermal neutron flux to the average epithermal flux and is therefore a characteristic of the particular reactor considered. This constant must be determined empirically; for ZPR-1 C was found to be 0.55.

Equation (1) was tested by a comparison of the measured and the calculated effectiveness for a number of control rod slabs, and the results are shown in Table 1.9.

TABLE 1.7—THERMAL NEUTRON ABSORPTION FACTOR

| $y = Nt\sigma_{th}$ | $1/2 F_1(y)$ |
|---------------------|--------------|
| 1 | 0.37 |
| 2 | 0.44 |
| 3 | 0.47 |
| 4 | 0.48 |

TABLE 1.8—EPITHERMAL NEUTRON ABSORPTION FACTOR

| $x = N\sigma(E)$ | $F_2(x)$ |
|------------------|----------|
| 1 | 1.2 |
| 2 | 1.8 |
| 3 | 2.2 |

TABLE 1.9—COMPARISON OF RELATIVE ABSORPTION EFFECTIVENESS [24]

| Control rod materials | | Absorption effectiveness | | |
|--------------------------|-----------------|--------------------------|------------------|----------|
| Alloy materials | Thickness (in.) | Calc | Exp ¹ | Calc/Exp |
| Hf + SS----- | Hf—0.10 | 0.533 | 0.545 | 0.98 |
| | SS—0.095 | | | |
| Hf + SS----- | Hf—0.15 | 0.617 | 0.607 | 1.02 |
| | SS—0.095 | | | |
| Hf----- | Hf—0.20 | 0.656 | 0.654 | 1.00 |
| Hf----- | Hf—0.025 | 0.686 | 0.680 | 1.01 |
| Hf + Cd + Hf----- | Hf—0.10 | 0.708 | 0.698 | 1.01 |
| | Cd—0.02 | | | |
| | Hf—0.10 | | | |
| Cd + Al + Cd----- | Cd—0.02 | 0.50 | 0.496 | 1.00 |
| | Al—0.15 | | | |
| | Cd—0.02 | | | |
| Co----- | Co—0.10 | 0.37 | 0.39 | 0.95 |
| Co----- | Co—0.20 | 0.47 | 0.49 | 0.96 |
| Co----- | Co—0.25 | 0.50 | 0.52 | 0.96 |
| Co (30%) + Ag (70%)----- | Co + Ag—0.10 | 0.590 | 0.556 | 1.06 |
| Cd (30%) + Ag (70%)----- | Cd + Ag—0.25 | 0.630 | 0.654 | 0.96 |
| Au----- | Au—0.10 | 0.521 | 0.546 | 0.95 |
| Au----- | Au—0.25 | 0.646 | 0.665 | 0.97 |

¹ From ZPR-1 (Zero Power Reactor—A water-moderated critical experiment).

As indicated in Table 1.9, the agreement between experimental values and values obtained with Eq (1) is within 1–2 percent for Hf and Hf + Cd-Ag composite rods, and within about 6 percent for Au, Cd-Ag, and Co rods. This agreement would not necessarily be true for a reactor in which the spectrum differed markedly from the simple expressions assumed for the equation.

1.3 NUCLEAR USES OF HAFNIUM

By W. H. Wilson ⁸

Hafnium is an excellent control rod material because of its neutron absorption properties, its corrosion resistance in hot water, and its

⁸ Naval Reactors, USAEC, Washington, D.C.

mechanical properties. Hafnium is unique in the extent to which it meets the requirements for a control rod material.

There are several ways in which a nuclear reactor may be controlled. The simplest method is to insert a neutron absorbing material into a reactor. It is also equally feasible, from a physics standpoint, to withdraw fuel from the reactor core such that the remaining fraction of the uranium fuel would not be critical and the reactor would not operate. However, moving fuel presents numerous design problems since the fuel must be adequately cooled when the reactor is operating.

General Discussion of Absorber Control Rods

The location of absorber control rods must be such that they can be easily moved. The position of one control rod in the center of a cylindrical reactor core is shown conceptually in Figure 1.3. Normally, the neutron flux decreases from the center to the edge of a reactor core due to the leakage of neutrons from the outer surface of the core as shown in Figure 1.4. Insertion of a central control rod changes the neutron flux as indicated in Figure 1.5.

Reactor control rods are generally long metallic blades which, when fully inserted in the reactor, absorb a sufficient number of

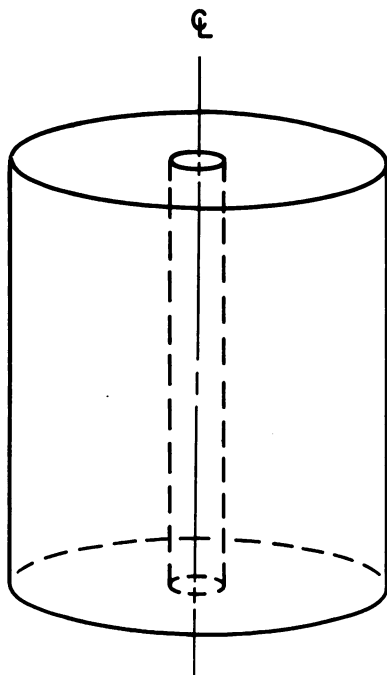


FIGURE 1.3. Control Rod in Center of Cylindrical Reactor Core.

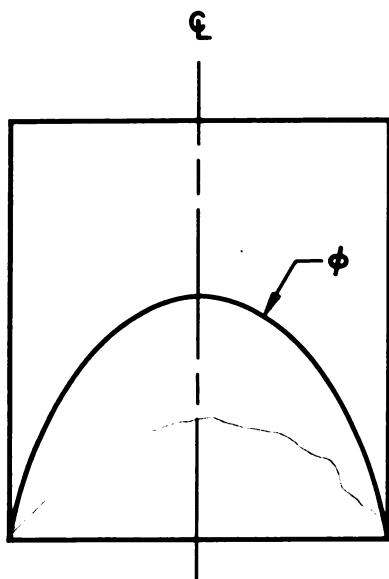


FIGURE 1.4. Neutron Flux without Control Rod.

neutrons to completely stop the nuclear chain reaction. Pulling the control rods out of the reactor decreases the number of neutrons absorbed by the control rods and makes many more neutrons available for absorption by the fuel. This causes the number of fissions to increase, and more neutrons are produced. When the control rods have been sufficiently removed, the number of neutrons produced by fissioning is equal to the number absorbed or lost from the system, and the reactor is said to be "critical" or self sustaining. At this point, if more neutron absorber is removed by control rod withdrawal, the neutron population will steadily increase at a rate which is a function of the amount of poison removed.

The power level, which is proportional to the neutron density, is allowed to increase to the desired value, and then the rods are again returned to the critical position to maintain the power at the chosen level.

Throughout core lifetime, the reactivity of the reactor core will change due to such effects as the depletion of fissionable atoms and burnable poison atoms and the buildup of fission product poisons. Thus, in order to compensate for these lifetime effects, it is necessary to move control rods throughout the life of the reactor. In particular, the control rods also serve to compensate for changing xenon concentrations in the core. The xenon, which is a strong neutron absorber, results from the decay of iodine atoms produced by fissioning of uranium atoms.

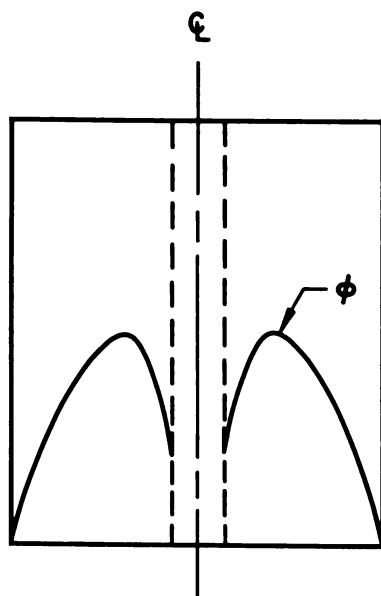


FIGURE 1.5. Neutron Flux with Control Rod.

Nuclear Effectiveness of Control Rod Materials

There are a number of elements with high neutron absorption cross sections which have been considered as possible control rod materials. The control worth of various materials is given in Table 1.10. As can be seen, combinations of elements are often more effective in controlling reactors than are the individual elements. Specifically, in the case of silver-indium-cadmium, the nuclear resonance absorption cross section of silver and indium augment each other so that neutrons are absorbed over a wide range of neutron energies, and the cadmium increases the effectiveness of the alloy for absorbing thermal neutrons. The result is that the alloy is superior as a control material to any one of its three constituent elements alone.

Hafnium is much more effective than is indicated by its thermal neutron cross section of 105 barns because of its ability to absorb neutrons above thermal energies. This effect, known as resonance energy absorption, roughly doubles the effectiveness of hafnium as a neutron absorbing material.

In addition, hafnium has a further favorable property as a control rod material in that its worth changes relatively slowly with irradiation; when a hafnium atom absorbs a neutron, a new, highly absorbing hafnium isotope will usually be formed. This resistance of hafnium to depletion is very fortunate.

TABLE 1.10—MEASURED CONTROL WORTH OF VARIOUS MATERIALS

| <i>Materials</i> | <i>Amount of principal poisons (w/o)</i> | <i>Worth relative to hafnium</i> |
|--|---|----------------------------------|
| Boron-stainless steel..... | 3.0% B ¹⁰ | 1. 13 |
| Boron-stainless steel..... | 2.0% B ¹⁰ | 1. 08 |
| Boron-titanium-hafnium..... | 1.0% B ¹⁰ | 1. 00 |
| Hafnium..... | | 1. 00 |
| Silver-indium-cadmium..... | 75% Ag, 20% In, 5% Cd. | 1. 03 |
| Boron-stainless steel..... | 0.97% B ¹⁰ | 0. 97 |
| Boron-titanium..... | 1.0% B ¹⁰ | 0. 96 |
| Eu ₂ O ₃ -stainless steel..... | 15% Eu ₂ O ₃ | 0. 94 |
| Indium..... | | 0. 93 |
| Silver-cadmium..... | 70% Ag, 30% Cd..... | 0. 92 |
| Silver..... | | 0. 88 |
| Cadmium..... | | 0. 88 |
| Gadolinium-titanium..... | 8.7% Gd..... | 0. 73 |
| Eu ₂ O ₃ -stainless steel..... | 4.1% Eu ₂ O ₃ | 0. 73 |
| Sm ₂ O ₃ -stainless steel..... | 2.7% Sm ₂ O ₃ | 0. 71 |
| Haynes-25 alloy..... | | 0. 66 |
| Titanium..... | | 0. 30 |
| Stainless steel (Type 304)..... | | 0. 24 |
| Aluminum (Type 2S)..... | | 0. 072 |
| Zircaloy-2..... | | 0. 049 |

Notes:

1. The control worth of any material is dependent upon the neutron spectrum of the reactor which, in turn, is a function of the reactor design parameters. The control worths given in the above table were measured in a critical assembly having a spectrum typical of many types of light water-moderated reactors containing highly-enriched uranium fuel.

2. Relative worths are based on 2 x 2 x 0.2-in. specimens.

3. Samples were measured in a slab critical assembly.

The ability of other materials to remain effective after long use is outside the scope of this book but will be covered fully in the forthcoming book on *Neutron Absorber Materials for Reactor Control* [25].

Other Properties of Control Rod Materials

In addition to the nuclear effectiveness discussed in the preceding section, it is necessary that useful control rod materials meet other requirements. These requirements may be particularly severe since the control rods are usually the only movable parts in the reactor core. A control rod must not bend or jam and must possess a high degree of corrosion resistance in order to limit the amount of radioactive material released to the reactor system by corrosion attack. It would be serious for a quantity of the poison material to be removed from the rods by corrosion since that could decrease the amount of available control in the core significantly. Plating or

cladding the poison material may not provide adequate corrosion protection since, if small manufacturing defects existed or if the surface protection were penetrated by rubbing, wearing, or erosion, exposure of the poison material to the coolant would result in loss of control rod material.

A number of considerations are involved in the mechanical design of control rods. The physical dimensions and the total number of control rods are arrived at by consideration of the nuclear design of the reactor as well as the mechanical design of the reactor core, the control rod drive mechanism, and the required penetrations of the pressure vessel head. It is necessary here to point out only the general nature of the mechanical design considerations for the control rod itself. Lateral temperature gradients exist in the control rod as a result of variations in gamma heat generation and cooling. These gradients, which cause the rod to distort, are minimized by assuring ample cooling capacity by the coolant passing around the rod and by avoiding nonuniform sections. Material properties favoring minimum thermal distortion are high elastic modulus, high thermal conductivity, low thermal expansivity, and low density. The control rod is normally supported only at the upper end. Therefore, deflection of the lower end could be appreciable if the flow of coolant past the rod were nonuniform. In this connection, a high elastic modulus is desirable. Gross deflections are prevented by the rubbing shoes located near the lower end of the rod. The rod is subjected to shock loading when it is scrammed. In this connection, a high yield strength and ductility are favorable, but it is necessary to resort to full-scale shock testing in order to establish the adequacy of the control rod. In mobile reactors both vertical and lateral shock can be imparted to the control rod.

The nuclear, strength, and corrosion properties must be retained during the life of the reactor core. This means that the high cross section isotopes must not deplete excessively during use and that the mechanical and corrosion properties must not be damaged excessively by corrosive attack or by irradiation. The availability and cost of the control rod material must be acceptable. The material must be capable of being fabricated to precise dimensions.

This section and the sections to follow reflect the fact that the principal application of hafnium is as a control rod material in water-cooled nuclear reactors. Use in other types of nuclear reactors would require different mechanical and corrosion properties. For example, higher strength at elevated temperature would, in general, be required for the control rod material in gas-cooled or liquid metal-

cooled reactors. To take advantage of the nuclear properties of hafnium in such a case, it may be necessary to develop hafnium alloys having the required mechanical properties and resistance to attack by the coolant or to use refractory compounds of hafnium.

Comparison of Control Rod Materials

There are very few materials which meet the requirements for a control rod material described thus far. A few pertinent properties of elements having high neutron absorption are listed in Table 1.11.

Lithium and mercury-rich materials have been dropped from consideration in mobile power reactors because no alloys or compounds have been found which are sufficiently stable to assure that the nuclear poison material would not escape from the reactor (thus increasing reactivity and raising power levels further) during certain reactor transients. Cadmium and indium cannot be used alone for the same reasons, but it has been found that these elements, when alloyed with silver, result in a sufficiently stable material to warrant consideration for control rods in water-cooled reactors. Considerations of price, availability, and very high induced radioactivity prevent serious consideration of gold, rhodium, rhenium, iridium, and cobalt.

Therefore, the elements listed in Table 1.11 which can seriously be considered for control rod application are boron, silver, silver alloys, rare earth elements, and hafnium.

Complete coverage of control rod materials is planned for the forthcoming book on *Neutron Absorber Materials for Reactor Control* [25]. However, the following section will show briefly how these four materials compare.

Boron Materials

Boron-containing materials of interest for control rods are alloys such as stainless steel-boron, dispersions of B_4C , and ceramic bodies such as high-density boron carbides. As indicated in Table 1.11, when boron absorbs a neutron, it releases an alpha particle and becomes lithium-7. The alpha particle is, of course, a helium nucleus.

Hence, for every boron atom destroyed, a helium atom is formed. In other words, if an alloy with one atom percent boron-10 is in a reactor long enough for all the boron atoms to absorb neutrons, the resulting material will contain one atom percent helium and one atom percent lithium. Diffusion of helium and nucleation and

TABLE 1.11—COMPARISON OF ELEMENTS HAVING HIGH NEUTRON ABSORPTION
[11, 26, 27, 28, 29]

| Element | Atomic number | Density | | Melting point (° C) | Crystal structure | High cross section isotope | Atomic abundance of isotope (%) | Thermal cross section (barns) | Microscopic thermal cross section (cm ⁻¹) | Neutron absorption reaction |
|---------------|---------------|---------|----------------------------|---------------------|-------------------|----------------------------|---------------------------------|-------------------------------|---|-----------------------------|
| | | (g/cc) | (10 ²² atom/cc) | | | | | | | |
| Lithium..... | 3 | 0.53 | 4.6 | 186 | bcc | Natural 6 | (100) 7.5 | 70 940 | 3.3 | n, alpha. |
| Boron..... | 5 | 2.3 | 14.0 | 2300 | ortho | Natural 10 | (100) 20 | 750 3800 | 97.0 | n, alpha. |
| Cobalt..... | 27 | 8.9 | 9.1 | 1495 | cph | 59 | 100 | 37 | 3.4 | n, gamma. |
| Rhodium..... | 45 | 12.4 | 2.3 | 1970 | fcc | 103 | 100 | 156 | 11.0 | n, gamma. |
| Silver..... | 47 | 10.5 | 5.9 | 960 | fcc | Natural 107 109 | (100) 51.35 48.65 | 63 31 87 | 3.7 | n, gamma. |
| Cadmium..... | 48 | 8.6 | 4.6 | 321 | cph | Natural 113 | (100) 12.26 | 2450 20,000 | 11.0 | n, gamma. |
| Indium..... | 49 | 7.3 | 3.8 | 156 | fcc | Natural 113 115 | (100) 4.23 95.77 | 196 58 207 | 7.5 | n, gamma. |
| Samarium..... | 62 | 7 | 3.1 | 1050 | rhombo | Natural 147 149 | (100) 15.07 13.84 | 5600 87 40,800 | 170.0 | n, gamma. |
| Europium..... | 63 | 5.2 | 2.1 | 900 | bcc | Natural 151 153 | (100) 47.77 52.23 | 4300 7700 400 | 88.0 | n, gamma. |

| | | | | | | | | | | |
|-----------------|----|-------|-----|------|--------|---------|---|------------------------------------|--------|-----------|
| Gadolinium..... | 64 | 7.9 | 3.1 | 1350 | cph | Natural | (100) 14.73 15.08 | 46,000 60,000 240,000 | 1390.0 | n, gamma. |
| Dysprosium..... | 66 | 8.6 | 3.2 | 1400 | cph | Natural | (100) 25.53 24.97 28.18 | 950 2600 | 30 | n, gamma. |
| Erbium..... | 68 | 9.1 | 3.3 | 1500 | cph | Natural | (100) | 170 | 5.6 | |
| Hafnium..... | 72 | 13.09 | 4.4 | 2222 | cph | Natural | (100) 5.15 18.39 27.08 13.78 35.44 | 105 15 380 75 65 14 | 4.6 | n, gamma. |
| Rhenium..... | 75 | 20 | 6.9 | 4170 | fcc | Natural | (100) 37.07 62.93 | 86 104 66 | 5.6 | n, gamma. |
| Iridium..... | 77 | 22.4 | 7.0 | 245 | fcc | Natural | (100) 38.5 61.5 | 440 960 130 | 31 | n, gamma. |
| Gold..... | 79 | 19.3 | 5.9 | 106 | fcc | | 100 | 98 | 5.8 | n, gamma. |
| Mercury..... | 80 | 13.5 | 4.1 | -39 | rhombo | Natural | (100) 10.0 16.8 | 380 2500 | 15 | n, gamma. |

Notes:

1. As pointed out and discussed in the text, the thermal absorption cross sections listed in this table do not constitute sufficient information to permit calculation or comparison of the control worths of the elements listed. Actual measurements of control worth of various materials are reported in this chapter.
2. bcc-body centered cubic; fcc-face centered cubic; cph-close packed hexagonal; fct-face centered tetragonal; ortho-orthorhombic; rhombo-rhomboidal.
3. "Natural" under the High Cross Section Isotope column refers to material with isotopic ratios which normally occur in nature.

growth of gas bubbles may produce swelling and cracking of the material. In addition, the presence of lithium in stainless steel or zirconium reduces corrosion resistance in high temperature water.

The problems connected with the formation of helium and lithium under irradiation seriously restrict the amount of boron which can be used and, hence, the nuclear effectiveness of the control rod material. Only about 0.5 percent boron-10 can be added to stainless steel (or about 0.2 percent to zirconium) before the material cracks and loses corrosion resistance upon irradiation. As can be estimated from Table 1.10, such materials are not as effective as hafnium. If such materials were used, more or larger rods would be required to provide the required amount of reactor control. Additional rods, with their driving mechanisms, power supplies, and electrical controls, add considerably to the cost and complexity of a power reactor. Larger rods would complicate the design of the reactor core and its pressure vessel and drive mechanism.

Silver Alloys

The development of the silver-indium-cadmium alloys offers the possibility of using materials which are more available than hafnium and have equal nuclear effectiveness. However, silver alloys have low creep strength and are not so corrosion resistant as hafnium in high temperature water. Furthermore, silver becomes very radioactive during use in a nuclear reactor, and any loss of material by corrosion or wear would release large quantities of radioactivity to the water coolant. Radioactive silver has a long half life and will emit radiation for a long time. It has been found that these silver alloys are not sufficiently corrosion resistant in high temperature water to warrant their use in mobile power reactors without cladding or similar protection.

Rare Earth Materials

Europium has excellent nuclear properties for control rod use; however, it is much more expensive than other possible control rod materials. The other rare earth elements with high cross sections—gadolinium, samarium, dysprosium, and erbium—do not have sufficient abundance of the highly absorbing isotopes to qualify as control rod materials for power reactors.

Hafnium Control Rods

Hafnium meets the requirements for a control rod material for water-cooled power reactors better than any other material investigated. The control effectiveness shown in Table 1.10 is not only

high, but remains relatively high throughout reactor life because of the initially high abundance of high cross section isotopes and because additional high cross section isotopes are formed.

The corrosion resistance of hafnium in hot water is exceptionally good. Unalloyed hafnium has a lower corrosion rate than the zirconium alloy Zircaloy-2 which is widely used because of its low corrosion rate. For example, the weight gains of these materials, corrosion tested for 44 days in 750° F steam, would be about 6 mg/dm² for unalloyed hafnium compared with about 48 mg/dm² for Zircaloy-2.

The yield strength of hafnium at 600° F is about the same as that of Zircaloy-2 (about 18,000 psi). This strength is adequate to permit design of hafnium control rods for use in water-cooled reactors and assure that the rods will not deform or jam during normal operation. The low modulus of elasticity (14×10^6 psi) is not detrimental because the large cross sections used in the design of control rods usually provide adequate stiffness to limit elastic bending even of long control rods.

Some difficulty is experienced in welding hafnium to zirconium because of the difference in the melting points. Additional difficulty is experienced in interpreting radiographs because of the marked difference in density. The fact that hafnium and zirconium have about the same thermal expansion coefficients means that welds of these two metals are not usually subject to severe thermal stresses. The ability to make strong welded joints of hafnium to zirconium is a distinct advantage. The inability to weld hafnium or zirconium to steels is a disadvantage and a mechanical joint is usually required somewhere between the hafnium control rod and the mechanism driving the rod. Details of the design, manufacture, and use of hafnium control rods for the PWR are contained in the book, *Shippingport Pressurized Water Reactor* [30].

Illustrated in Figure 1.6 is a hafnium control rod used in the Shippingport Pressurized Water Reactor. The active length of the rod is 71½ inches. The location of the weld joining the 3½-inch Zircaloy-2 cruciform extension to the top end of the hafnium section is clearly visible in the photographs. The rubbing shoes near the bottom end of the control rod are for the purpose of preventing gross misalignment of the control rod in the control rod channel. Those shown in Figure 1.6 are raised portions of the parent rod material formed by a coining operation. Figure 1.7 is a view of the top of a PWR seed fuel element cluster showing the cruciform control rod channel.

The first use of hafnium as a control rod material came about in an interesting way. In 1950, when a water-cooled reactor using zirconium was chosen for the *Nautilus*, the proposed control rods

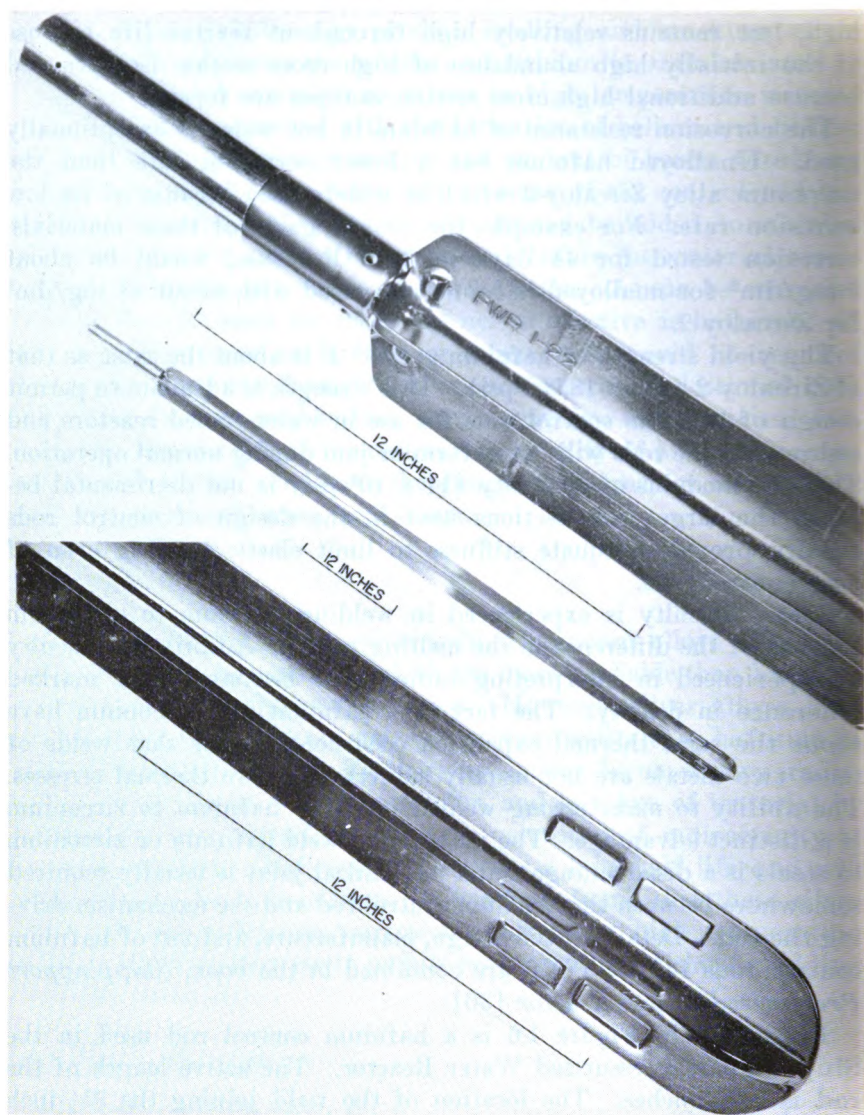


FIGURE 1.6. Hafnium Control Rod for the Shippingport Pressurized Water Reactor.

were 30 percent cadmium—70 percent silver alloy clad with stainless steel. However, during thermal cycling tests of the clad rods in 1951, the cladding failed by blistering, indicating that the stainless-to-silver-alloy metallurgical bond was not sufficiently strong to withstand the stresses arising from differential thermal expansion of stainless steel. There appeared to be no satisfactory way to correct

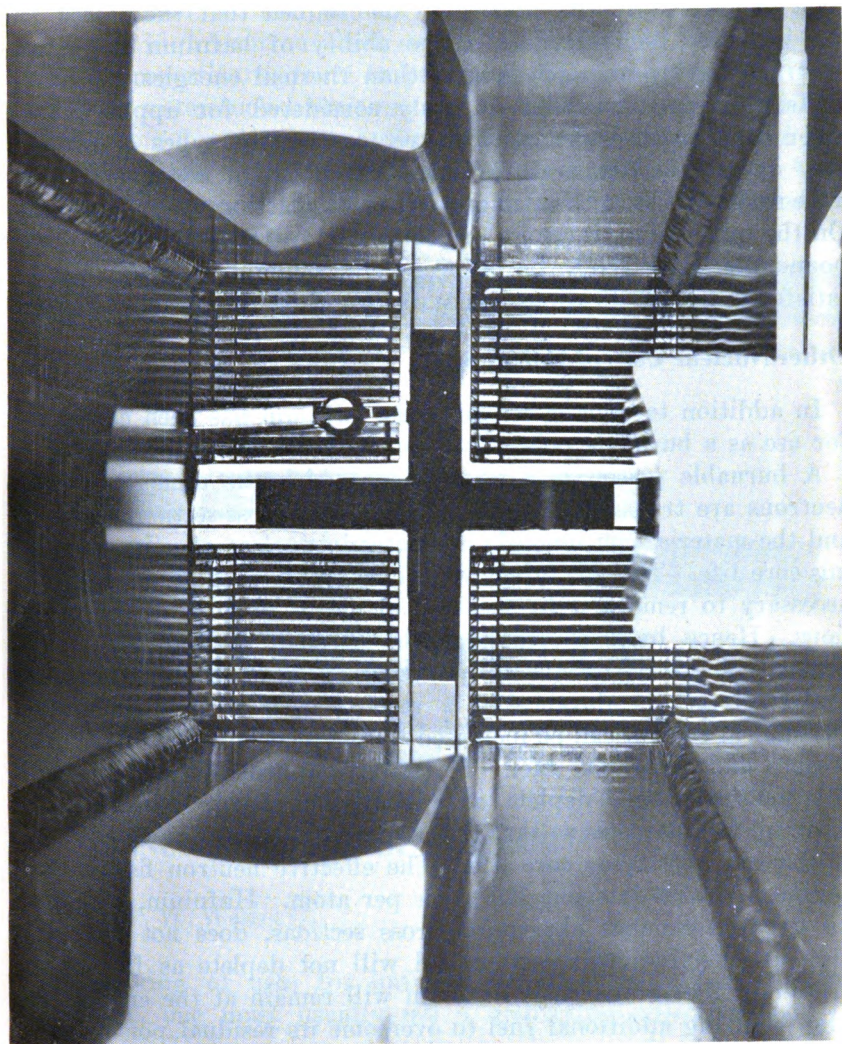


FIGURE 1.7. View of the Top of a Seed Cluster of the Shippingport Pressurized Water Reactor Showing the Cruciform Control Rod Channel.

this deficiency, and it was necessary to find an alternate control rod material. Fortunately, some hafnium metal had been produced, and the nuclear and structural properties indicated that hafnium would be satisfactory. Insertion of hafnium blades in the nuclear mockup of the *Nautilus* reactor (called the ZPR—Zero Power Reactor) indicated that hafnium was even better than had

been expected. It has since been determined that the reason for the increased control effect is the ability of hafnium to capture neutrons having energies greater than thermal energies.

Hafnium has not been seriously considered for application to other than water-cooled nuclear reactors. Some types of reactors may operate at temperatures such that hafnium metal would not have sufficient strength or might not resist reaction with the coolant. On the other hand, ceramics or cements of refractory hafnium compounds, such as HfO_2 , or hafnium alloys might well prove to be satisfactory in applications where unalloyed hafnium cannot be used.

Other Nuclear Uses of Hafnium

In addition to reactor control rods, hafnium has been considered for use as a burnable poison and as a neutron flux depressor.

A burnable poison is a material in which the atoms absorbing neutrons are transmuted to nonpoison (low cross-section) isotopes, and the material continuously decreases in nuclear effectiveness during core life. The advantage of a burnable poison is that it is not necessary to remove it by mechanical means during reactor operations. Hence, by employing burnable poisons, the total amount of poison which must be moved by mechanical means can be decreased. Conversely, the endurance of a reactor with a fixed amount of mechanical control can be increased by the incorporation of burnable poisons and additional fuel. To the first approximation, the burnable poison should deplete at a somewhat faster rate than the uranium fuel depletes so that the nuclear poison will be nearly gone at the end of reactor core life. The effective neutron fission cross section of U-235 is about 700 barns per atom. Hafnium, even with its strong resonance absorption cross sections, does not have this high an effective cross section and will not deplete as fast as the uranium. Therefore, some hafnium will remain at the end of core life, requiring additional fuel to overcome its residual poison effect. However, despite this disadvantage, hafnium may be a useful burnable poison for very long life reactor cores because at the end of core life the poisoning effect of the hafnium residue decreases relative to the poison effect of the fission products as core lifetimes are increased.

A flux depressor is a material strategically placed in a reactor to absorb neutrons at a particular point. By this means, the neutron flux at this point can be depressed. Hence, the peaks in neutron flux can be decreased, and the over-all ratio of maximum to average neutron flux distribution may be improved. Such neutron flux peaks may be caused by the presence of local high concentrations of water in the core [such as when a control rod is withdrawn and the water (coolant and moderator) replaces the withdrawn control rod]. Many

materials could be used as flux depressors, but hafnium with its sufficiently high neutron cross section, and excellent chemical and physical properties, appears to be a useful flux depressor material for use in water-cooled reactors. One experimental application of hafnium as a flux depressor is the use of hafnium sheet around fuel element samples tested in the Engineering Test Reactor at Arco, Idaho. A picture of the fuel element samples and flux depressors is shown in Figure 1.8.

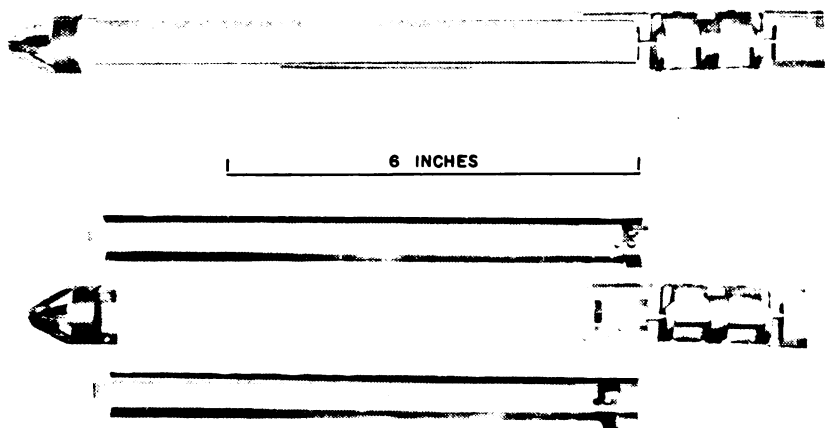


FIGURE 1.8. Fuel Element Samples with Hafnium Flux Depressor in Place (top) and Removed (bottom).

1.4 NONNUCLEAR USES OF HAFNIUM

By F. W. Wessel⁹

In speaking of uses for hafnium outside the field of nuclear technology, one must usually use a qualifying adjective such as "potential." Hafnium has not become available except as a byproduct of zirconium production. While commerce in hafnium has not been sufficient to permit a price pattern to form, the selling price of hafnium crystal bar produced in excess of that associated with zirconium production might be many times the price of reactor-grade zirconium sponge.

Three types of applications are discussed below: (a) those in which hafnium has been experimentally successful, (b) those in which hafnium might be expected to be successful on the basis of its known properties, and (c) those few already successful applications employing modest amounts of hafnium. Some of the properties of hafnium and hafnium compounds are listed in Table 1.12.

⁹ U.S. Bureau of Mines, Department of Interior, Washington, D.C.

Metallic Hafnium

Hafnium has been successfully used in two ways as a component of electric light filaments; first, it has been employed in the pure state as a filament in gas-filled bulbs [31], and second, it has been used to alloy with tungsten to increase the strength of the filament [32].

TABLE 1.12—PROPERTIES OF HAFNIUM AND HAFNIUM COMPOUNDS [33]

| | Molecular weight | Melting point (° C) | Crystal form | Density |
|--------------------------|------------------|---------------------|-------------------------------|---------|
| Hf..... | 178. 5 | 2222 | Hexagonal close packed..... | 13. 09 |
| HfO ₂ | 210. 5 | 2810 | Monoclinic ¹ | 9. 68 |
| HfC..... | 190. 6 | 3890 | Cubic..... | 12. 2 |
| CaHfO ₃ | 266. 5 | 2470 | Orthorhombic..... | 5. 73 |
| HfSiO ₄ | 270. 5 | ----- | Tetragonal..... | ----- |

¹ Up to 1700° C.

Like its sister metals titanium and zirconium, hafnium is effective as a “getter” in vacuum tubes to scavenge traces of oxygen and nitrogen [34]. For this purpose, it is sometimes used as an alloy with titanium; for satisfactory performance the alloy should be free of oxygen, nitrogen, carbon, and silicon [35].

Its high melting point and emissivity suggest its use in cathode-ray tubes and as an electrode in rectifiers and high pressure discharge tubes, both as a solid metal part and as a sprayed-on surfacing material. For the latter use it has been alloyed with tungsten or molybdenum [34, 35, 36].

It improves the properties of nickel-chromium resistance wire when added as a minor constituent [35].

Hafnium powder, like zirconium powder, may be used as a component of flash powders and pyrotechnics and as a component of primers in detonating caps and ammunition [32].

Hafnium has been successfully alloyed with iron, nickel, cobalt, copper, silver, aluminum, titanium, and zirconium in various amounts, but attempts to alloy it with lead or tin were unsuccessful [32].

When rubbed on unglazed porcelain, it abrades readily to form a bright, adherent coating and thus can be used for ceramic decoration [32].

Over the past 30 years, several patents have been issued on materials containing hafnium as an alloying addition, but none seems to have shown particularly promising properties. Recently, hafnium has been considered as an alloy addition in connection with refractory

metallurgy. An alloy of particular promise is niobium with 1 w/o Hf-1 w/o Ti-1 w/o Zr, which has a yield strength at 1,093° C of 43,200 psi [37].

Hafnium Oxide

In the range of 1,600 to 1,700° C, hafnium oxide (HfO_2) undergoes the same inversion from the monoclinic to the tetragonal system as does zirconia between 1,000 and 1,100° C. Its shrinkage upon conversion is 3.4 percent compared with 7.5 percent for zirconia [33]. Thus it appears that the life of hafnia would exceed that of zirconia when used for refractory duty. This, in itself, is not likely to overcome sufficiently the effect of hafnia's high price to create anything more impressive than a small, highly specialized demand.

In the production of pure tungsten for use in incandescent filaments, grain growth may be excessive. To inhibit this, a small quantity of hafnium nitrate may be added during the reduction of tungsten trioxide to metal. The process converts the nitrate to oxide, which remains to the extent of 0.1 to 3.0 percent as harmless inclusions within the metallic tungsten [39, 40, 41]. For this purpose, however, thorium salts are currently used.

Hafnia may have some application as a catalyst in high temperature organic reactions [31]. The dehydration of ethyl alcohol and the acylation of thiophene are two examples [38].

Much research has been conducted by Siemens and Halske A-G in Germany to establish the conditions for use of hafnia in ceramic bodies. Several patents cover this work [39]. Such refractories would, of course, be most valuable in high temperature applications.

Hafnia, either as a loose grain or in shaped pieces, may have some potential as a heat insulator [31].

Like zirconia, hafnia may be used as an opacifier in enamels and glazes [32].

A special optical glass, used in high temperature service, requires hafnium oxide as an important constituent [32, 35].

Hafnium Silicate

Hafnium silicate (HfSiO_4) occurs in nature only as a portion of the zircon (zirconium silicate) lattice. However, it has been synthesized [33], and its properties are quite similar to those of natural zircon.

Zircon is itself used as a refractory, principally by the glass and aluminum industries, and here the presence of hafnium silicate improves the performance of the zirconium silicate. The latter, when pure, softens in the range of 1,550–1,750° C, and any addition of hafnium silicate tends to raise this softening temperature [33, 42, 43].

Since the linear expansion coefficients of the two silicates are quite similar, no difficulty is thereby introduced with the hafnium.

Hafnium silicate also finds use as a catalyst in the dissociation of various aryl compounds [39].

Calcium Hafnate [33]

The volume change accompanying the inversion of both hafnia and zirconia can be avoided, to a great extent, by "stabilizing" with alkaline-earth oxides. In this process, alkaline-earth hafnates and zirconates may be formed by heating the silicate with limestone or dolomite in a rotary kiln at 2,600° F; alternatively, they may also be formed by sintering a mixture of oxides.

The calcium hafnate thus formed is orthorhombic. Hafnia plus 8 percent lime forms a face-centered cubic lattice stable to at least 1,700° C. The lattice parameter increases with increased lime addition up to 20 mol percent, but additions much in excess of 8 percent cause a decrease in the softening temperature and a loss in resistance to thermal shock.

The binary CaO-HfO_2 diagram has not yet been established, but sufficient work has been done to determine that it is similar to the CaO-ZrO_2 diagram and that compositions in the range mentioned remain within a large terminal solid solution field.

It may be concluded that, while calcium hafnate in the pure state has a melting point somewhat higher than refractories in common use, its employment as the minor component of a calcium hafnate-hafnium oxide mixture provides for an even higher melting point, greater strength at high temperature, and almost complete elimination of volume change at the inversion temperature.

Hafnium Carbide

Hafnium carbide (HfC) is a compound with a density of 12.20 g/cc and a melting point of 3890° C—the highest encountered among the simple carbides [33, 43]. Although development is still in the laboratory stage, it is clear that this material will make an excellent high-temperature refractory, with the single drawback of low impact resistance at elevated temperatures [44].

A double carbide of hafnium and tantalum (HfC-4TaC) has been developed and has the highest melting point of any ceramic material, 3942° C [31].

Hafnium carbide is an extremely hard material, and its potential as a substitute for industrial diamond was investigated [45]. It was found to be unsuited for such applications, but nevertheless hard enough to be of some value as an insert in cutting tools and as a grinding medium [44, 45].

A German patent describes the use of hafnium carbide as a filament in certain types of electric lamps [39].

Hafnium Nitride and Hafnium Boride

These compounds are newly developed and have not emerged from the laboratory. They have melting points of 3,300° C and 3,060° C, are highly conductive at high temperature, and may prove to have uses based on these properties [31].

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Chapter 2

EXTRACTION OF HAFNIUM FROM ORES

K. C. LI,¹ *Editor*

2.1 THE OCCURRENCE OF HAFNIUM MINERALS AND ORES

By H. W. Miller¹

The chemical similarity of hafnium to zirconium is so remarkable that its presence in minerals and chemically purified compounds of zirconium was not even suspected for many years. Since hafnium never occurs in minerals independently of zirconium, any discussion of the mineralogical occurrence of hafnium is at the same time a discussion of the occurrence of zirconium. This constitutes one of the finest known examples of the effect of the lanthanide contraction on elements separated by this inner transition series. Even though the atomic number of hafnium is much greater than that of zirconium, its ionic radius is nearly identical, and it fits easily into the crystal lattice of various zirconium minerals and compounds. This is, perhaps, the principal reason why the element hafnium always occurs in minerals of zirconium.

The Occurrence of Hafnium Minerals

Hafnium minerals are found in pegmatites, as a product of magmatic segregation, in contact metamorphic rocks, in dynamic regional metamorphic rocks [1], and finally, through the process of weathering, in placer deposits and various sedimentary formations.

Since hafnium and zirconium are nearly quantitatively concentrated in the silicate phase of meteorites, they can be considered to be lithophile in nature. The average content of zirconium in calc-alkalic igneous rocks, as calculated by de Hevesy and Wüerstlin, is presented in Table 2.1 [2].

TABLE 2.1—CONTENT OF ZIRCONIUM IN CALC-ALKALIC IGNEOUS ROCKS [2]

| <i>Mineral</i> | <i>Zirconium (grams/ton)</i> |
|---------------------------|----------------------------------|
| Peridotites, dunites..... | 60 |
| Gabbros..... | 140 |
| Diorites..... | 280 |
| Granites..... | 460 |

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The hafnium content of these rocks will probably be within the range of 0.5–1.5 percent of the zirconium content and, therefore, will reach a maximum of about 7 grams per ton.

Zircon is more characteristic of nepheline syenite pegmatites than granite pegmatites. Since the average content of hafnium in minerals of alkalic rocks is lower than those of calc-alkalic rocks, zircon found in nepheline syenites always contains less hafnium than that found in granites. The average Hf/Zr ratio of minerals from nepheline syenite rocks and from granitic rocks is presented in Table 2.2 [3].

TABLE 2.2—AVERAGE Hf/Zr RATIO OF MINERALS [3]

NEPHELINE SYENITE MINERALS

| <i>Mineral</i> | <i>Hf/Zr Ratio</i> |
|-------------------------|------------------------|
| Baddeleyite..... | 0.014 |
| Baddeleyite, favas..... | 0.008 |
| Catapleite..... | 0.011 |
| Elpidite..... | 0.011 |
| Eudialyte..... | 0.011 |
| Polymignite..... | 0.023 |
| Rosenbuschite..... | 0.017 |
| Wöhlerite..... | 0.034 |
| Zircon..... | 0.017 |

GRANITIC MINERALS

| | |
|-------------------|------|
| Alvite..... | 0.13 |
| Cyrtolite..... | 0.46 |
| Malacon..... | 0.08 |
| Naëgite..... | 0.46 |
| Thortveitite..... | 0.57 |
| Zircon..... | 0.05 |

Even though hafnium and zirconium are considered to be trace elements, their occurrence is world-wide. Zircon has been found in certain rocks to such an extent that it has even been considered as one of the rock forming minerals. Although zircon favors such crystalline rocks as syenites and granites, it occurs in a large variety of rock types. Zircon has been found in such volcanic rocks as quartz porphyry, phonolite, dolerite, trachyte, tephrite, dibase, and basalt [4]. It has been found in sedimentary rocks such as limestone, sandstone, and conglomerates and in metamorphic rocks such as slate, phyllite, schist, quartzite, marble, and gneiss.

The Abundance of Hafnium

Careful analyses of rocks and minerals have shown that the abundance ratio of hafnium to zirconium fluctuates within very narrow limits. This ratio has been determined to be about 0.02 in

the earth's crust. It is believed that no separation of hafnium from zirconium takes place in nature. This is probably true after the mineral has been formed; however, it is likely that during the process of fractional crystallization from the magma, certain conditions can influence the zirconium-hafnium ratio to a marked degree.

Although it has been stated that the concentration of hafnium in minerals never exceeds that of zirconium [5], Goldschmidt [6] reports that exceptional ratios between hafnium and zirconium have been observed in the mineral thortveitite, $(Y, Sc)_2 Si_2 O_7$. This mineral usually contains several percent of a mixture of zirconium and hafnium due to the fact that these ions may replace scandium in the thortveitite lattice. Substitution of hafnium for scandium is possible since their ionic radii are similar ($r = Zr^{+4}$ 0.87 Å, Hf^{+4} 0.86 Å, and Sc^{+3} 0.83 Å). It appears, from the work of de Hevesy, that in the case of the Norwegian thortveitite, the weight percent of hafnium exceeds that of zirconium. The Hf/Zr ratio for this mineral was determined to be 1.9 [7]. The similarity in size of the ionic radii of hafnium and scandium apparently favors the capture of hafnium in the thortveitite lattice even though the atomic concentration of zirconium was undoubtedly much greater in the original magma. This phenomenon is also responsible for the high hafnium-zirconium ratio in scandium-bearing wolframites.

O. I. Lee [8] prepared a list of zirconium minerals which were known to contain hafnium. This list is reproduced, in part, and presented in Table 2.3.

TABLE 2.3—LIST OF ZIRCONIUM MINERALS KNOWN TO CONTAIN HAFNIUM [8]

| <i>Mineral</i> | <i>ZrO₂</i> (Percent) | <i>HfO₂</i> (Percent) |
|----------------------|-------------------------------------|-------------------------------------|
| Baddeleyite..... | 98.9 | 1.2 |
| Catapleite..... | 31.5 | 0.3 |
| Elpidite..... | 20.28 | 0.2 |
| Eudialyte..... | 14.32 | 0.17 |
| Var. Eucolite..... | 12.21 | 0.2 |
| Polymignite..... | 29.11 | 0.6 |
| Rosenbuschite..... | 19.80 | 0.3 |
| Thortveitite..... | 2.0 | 0.5 |
| Var. Befanamite..... | 1.3 | 1.0 |
| Wöhlerite..... | 15.61 | 0.5 |
| Zircon..... | 64.23 | 2.0 |
| Var. Hyacinth..... | 64.83 | 1.2 |

ALTERED ZIRCONS

| | | |
|----------------|-------|-----|
| Alvite..... | 41.98 | 4.6 |
| Cyrtolite..... | 52.4 | 5.5 |
| Malacon..... | 65.18 | 3.4 |
| Naëgite..... | 49.8 | 3.5 |
| Zirkelite..... | 21.89 | 1.0 |

The highest hafnium content in minerals that have been investigated up to this time is presented in Table 2.4. These data are based on information obtained from papers by de Hevesy [9], de Hevesy and Wüerstlin [10], and Lee [8].

TABLE 2.4—MAXIMUM CONTENT OF HfO_2 IN ZIRCONIUM MINERALS [8, 9, 10]

| <i>Mineral</i> | <i>Formula</i> | <i>HfO₂</i> (Max w/o) |
|------------------|--|-------------------------------------|
| Zircon..... | ZrSiO_4 | 6.0 |
| Naëgite..... | $\text{ZrO}_2 \cdot \text{SiO}_2$ (Y, Th, Nb, Ta)..... | 7.0 |
| Malacon..... | $3 (\text{SiO}_2 \cdot \text{Zr, HfO}_2) \cdot \text{H}_2\text{O}$ | 4.0 |
| Cyrtolite..... | R_3Y_2 (Zr, Hf) $(\text{SiO}_4)_{12}$ | 10.0 |
| Alvite..... | $(\text{Zr, Hf, Be, Th})\text{O}_2 \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$ | 15.0 |
| Baddeleyite.... | ZrO_2 | 1.2 |
| Thortveitite.... | $(\text{Sc, Y})_2 \text{Si}_2\text{O}_7$ | 1.1 |

The highest concentrations of hafnium occur in certain altered zircons, as for example, naëgite, cyrtolite, malacon, and alvite. Since zircon contains an average of less than 2 percent hafnium [10], it is probable that the unusually high percentage of hafnium, as given in Table 2.4, is the result of contamination with one or more of the altered zircons.

Zircon crystals occurring in nepheline syenites and related rocks and their pegmatites are surprisingly resistant towards hydrothermal alteration in contrast to the altered zircons occurring in granite pegmatites. These altered zircons are not only richer in hafnium, but contain such elements as yttrium and associated lanthanides, thorium, uranium, phosphorous, niobium, and beryllium in amounts of several percent. In general, minerals with a high hafnium-to-zirconium ratio are more strongly radioactive than those with a lower content of hafnium. Piutti [11] reported that, in the case of zircon, the amount of hafnium present is proportional to the amount of radioactivity. De Hevesy [12], however, was unable to find a direct relationship between the radioactivity and the hafnium content of zircon. The radioactivity is due to the inclusion of thorium and uranium in the crystal lattice as a result of their concentration in the mother liquors of the granitic magmas in which enrichment of hafnium took place. In every case, the original crystal structure of the altered zircon has deteriorated due to the radioactivity of the occluded thorium and uranium.

In zirconium minerals of nepheline syenites, the weight percent of hafnium to zirconium varies from 0.5 percent to 1.5 percent and in granitic rocks it is often much higher than 4 percent. In non-quartzose or basic residual phonolites and nepheline syenites, higher percentages of zirconium have been reported. In certain rocks of the nepheline syenite family, the amount of zirconium and hafnium rises to above 1 percent, and in some special types, such as sodalite

syenites, which contain zirconium minerals (eudialyte, etc.), the amount has been reported as high as 10 percent. Occasionally, these sodalites and nepheline syenites may contain enough eudialyte to afford a source of commercial ore. Unfortunately, however, the most important zirconium resources of the earth are relatively poor in hafnium.

Minerals and Ores of Hafnium

Appreciable quantities of hafnium are found only in the altered zircon minerals such as cyrtolite, malacon, alvite, and naëgite. Of these, cyrtolite is by far the most common. Until recently there were no known commercial deposits of any of these minerals, and the hafnium industry depended upon the large scale mining of the more common "hafnium-poor" zirconium ores. Since zircon and baddeleyite form immense placers, they are the only important ore minerals of zirconium. The hafnium content of the ore from these sources, however, never exceeds 2 percent.

The only known commercial source of altered zircon occurs as a byproduct of columbite and tin mining operations in Nigeria. The zircon itself constitutes 70 percent of one byproduct fraction with a hafnium oxide content of $3\frac{1}{2}$ –5 percent. Approximately 2,400 tons of such byproduct is produced annually.

It is also possible that hafnium may be found in some presently unexpected source. A few years ago, it was reported that a considerable deposit of orthite was found in Tanganyika Territory, which assayed as high as 8 percent hafnium [13]. There has been no official confirmation of this unexpected mineral association [14].

Cyrtolite has been found in small quantities in the pegmatites of Colorado, Connecticut, California, Massachusetts, New York, North Carolina, and Texas. It has also been reported to occur in Canada, India, Norway, Sweden, and Russia. Alvite has been reported from a few localities in Norway, malacon from Madagascar, and naëgite from Japan. Baddeleyite has been reported in small quantities from near Bozeman, Montana; Mt. Somma, Italy; Kila, Belgian Congo; and in immense deposits in Brazil. Zircon is world-wide in occurrence [8, 15–21] and has been found in large quantities in the beach sands of Australia, India, and the United States, as well as in numerous stream placer deposits.

The largest amount of zircon comes from Australia, followed by India and Brazil. The baddeleyite ores of Brazil have been reported to assay as high as 93 percent ZrO_2 and 1.2 percent HfO_2 . The nepheline-bearing rocks of the Pocos de Caldas Plateau in Brazil contain huge quantities of zircon which is mined as zirconium ore. These rocks and the zircon placers derived therefrom are probably the greatest source of zirconium known today.

In the United States, zircon is obtained commercially as a co-product with rutile, ilmenite, and monazite. These minerals are mined by dredging the beach sands and stream placers of Florida, North Carolina, and Idaho.

A list of zirconium minerals, as taken from a paper by O. I. Lee [8], is reproduced in Table 2.5. Many of these minerals were not analyzed for hafnium, and all percentages given are the maximum values obtained at the time the list was compiled.

TABLE 2.5—ZIRCONIUM AND HAFNIUM MINERALS

| Mineral | Formula | ZrO ₂ Percent | HfO ₂ Percent |
|-----------------|---|-----------------------------|-----------------------------|
| Astrophyllite | (K, Na, H) ₉ (Fe, Mn, Ca, Mg) ₉ (Fe, Al)·[(Ti, Zr)(O, F ₂) ₃ (SiO ₄) ₉ | 4.97 | — |
| Baddeleyite | ZrO ₂ | 98.9 | 1.2 |
| Beckelite | Ca ₃ (Y, Ce, La, Nd, Pr) ₄ (Si, Zr) ₃ O ₁₅ | 2.5 | — |
| Catapleite | (Na ₂ , Ca)O·ZrO ₂ ·3SiO ₂ ·2H ₂ O | 31.53 | 0.3 |
| Chalcolamprite | RNb ₂ O ₆ F ₂ RSiO ₃ (R=Ce, Na, Zr, Ca) | 5.71 | — |
| Elpidite | Na ₂ O·ZrO ₂ ·6SiO ₂ ·3H ₂ O | 20.58 | 0.2 |
| Endeiolite | RNb ₂ O ₆ (OH) ₂ CeSiO ₃ (R=Na ₂ , Ca) | 3.78 | — |
| Eudialyte | (Na, Ca, Fe) ₆ Zr(OH, Cl)(SiO ₃) ₆ | 14.32 | 0.2 |
| Eucolite | (Na, Ca, Fe) ₆ Zr(OH, Cl)(SiO ₃) ₆ | 12.21 | 0.2 |
| Guarinite | 3CaSiO ₃ [Ca(F, OH)]NaZrO ₃ | 19.70 | — |
| Hiortdahlite | 6(Ca ₂ Si ₂ O ₆)·2(Na ₂ Ca, H ₂) ₂ ·(Zr ₂ F ₂ O ₄)·2/3 [Ca(Mg, Fe, Mn)·(Zr, Ti, Si) ₂ O ₆] | 21.48 | — |
| Johnstrupite | Na ₃ Ca ₈ Ce ₂ (F, OH) ₇ (SiO ₃) ₉ | 2.84 | — |
| Lävenite | Na(Zr, O, F)(Mn, Ca, Fe)(SiO ₃) ₂ | 28.9 | — |
| Leucosphenite | BaSi ₄ O ₆ ·2Na ₂ (Ti, Zr)Si ₃ O ₈ | 3.5 | — |
| Loranskite | (Tantalate of Y, Ce, Zr, Fe, etc.) | 20.0 | — |
| Lorenzenite | Na ₂ (Ti, Zr) ₄ O ₉ ·Na ₂ Si ₄ O ₉ | 11.92 | — |
| Mosandrite | (Same as Johnstrupite) | 7.43 | — |
| Nohlite | (Niobate of U, Y, Fe, etc.) | 2.96 | — |
| Oliveiraite | (Altered Euxenite) | 63.36 | — |
| Orvillite | 8ZrO ₂ ·6SiO ₂ ·5H ₂ O | 68.04 | — |
| Polymignite | 5RTiO ₃ ·5RZrO ₃ ·R(Nb, Ta) ₂ O ₆ (R=Ce, Fe, Ca) | 29.11 | 0.6 |
| Pyrochlore | CaNb ₂ O ₆ ·NaF | 2.90 | trace |
| Riebeckite | 4Na ₂ SiO ₃ ·5FeSiO ₃ ·5Fe ₂ Si ₃ O ₉ | 4.7 | trace |
| Rosenbuschite | 6CaSiO ₃ ·2Na ₂ ZrO ₂ F ₂ Ti·(SiO ₃)(TiO ₃) | 19.80 | 0.3 |
| Soda-Catapleite | Na ₂ O·ZrO ₂ ·3SiO ₂ ·2H ₂ O | 30.80 | — |
| Thortveitite | (Sc, Y) ₂ Si ₂ O ₇ | 2.0 | 0.5 |
| Befanamite | ScSi ₂ O ₇ | 1.3 | 1.0 |
| Uhligite | 3Ca(Ti, Zr) ₂ O ₅ ·Al ₂ TiO ₅ | 21.95 | — |
| Wöhlerite | 13(Ca, Na ₂)O·9SiO ₂ ·3ZrO ₂ ·Nb ₂ O ₅ | 15.61 | 0.5 |
| Zircon | ZrSiO ₄ | 64.23 | 1.98 |
| Alvite | (Zr, Hf, Th, Y, Be)SiO ₄ | 41.98 | 4.6 |
| Cyrtolite | Na ₂ Y ₂ (Zr, Hf)(SiO ₄) ₁₂ | 52.4 | 5.5 |
| Malacon | 3(SiO ₂ ·Zr, HfO ₂)·H ₂ O | 65.18 | 3.4 |
| Naëgite | ZrO ₂ ·SiO ₂ (Y, Th, Nb, Ta) | 49.8 | 3.5 |
| Zirkelite | (Ca, Fe)O·2(Zr, Ti, Th)O ₂ | 51.89 | 1.0 |

2.2 MINING AND ORE DRESSING METHODS

By H. W. Miller¹

At the present time economical mining of zircon can only be carried out by dredging or by strip mining methods. Conventional stripping equipment, bucket lines, and suction or dragline dredges are in use. After the excavated sands or gravel have been screened they may be concentrated by jigs, tables, riffles, or spirals. The process and equipment used depends to a great extent upon the associated minerals found in the heavy sands. Since zircon is only a co-product, secondary consideration is given to its separation. Magnetic and electrostatic separation methods are generally employed to segregate zircon and its associated minerals. The zircon is collected in the rejects or the tailings. As a rule, only one more simple gravity concentration step is required to obtain a high-grade product.

In Idaho, zircon is obtained as a byproduct of the monazite operations [22]. Dredging is carried out by means of a conventional bucket line operating against the bank of the dredging pond. After the buckets discharge onto tumblers, a trommel discards all material above one-fourth inch in size. The fines are put through parallel batteries of "rougher" jigs, and the hutch product from these jigs is then pumped to a dewatering cone. The concentrates are dewatered and shipped to the separating plant, where they are dried in a rotary kiln, passed over electrostatic and magnetic separators, and finally over an induced magnetic roll. The zircon and silica remain in the tailings while such minerals as ilmenite, magnetite, and monazite are removed. The zircon is easily separated from the silica by conventional shaking gravity tables.

The beach sands of Florida are mined by means of a floating suction dredge. The sands are pumped to a battery of Humphreys spirals, and the resulting concentrates are put through electrostatic separators. Finally magnetic separators and gravity concentrating tables are used to purify the product [23].

2.3 CONVERTING THE ORE

By J. H. McClain¹

This section deals with the preparation of a feed material suitable for introduction into a hafnium-zirconium separation system. While there are several methods of accomplishing this, the most important or most widely employed process involves converting the ore in an arc furnace to produce zirconium carbide followed by chlorination of

¹ Wah Chang Corp.

the carbide to form the tetrachloride. The tetrachloride is then suitable for feed material to either the hexone-thiocyanate or the tributyl phosphate-nitric acid separation systems.

No attempt is made to include those processes not directly applicable to metal production. To do so would be duplicating unnecessarily the effort of more comprehensive works such as Marden and Rich [24], Venable [25], and others.

In the production of zirconium and hafnium metal the most used ore is zircon. This is largely because of the ready availability and low cost of zircon as byproduct of rutile, monazite, and ilmenite mining operations. For this reason the total hafnium metal production is equivalent to roughly 2.1 percent of the total zirconium production, the natural proportion of hafnium to zirconium in usual zircon ores. Actually, no more than 1.5–1.8 percent is realized because of losses in the separations.

Zircon is attacked by fusion, carbothermic reaction, or high temperature chlorination to break the silicate bond and otherwise prepare it as feed material to the hafnium-zirconium separation system. Figure 2.1 illustrates the various methods and stages employed to process hafnium from ore to metal.

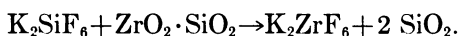
Fusion

G. de Hevesy, in early research [26], employed fusion of zircon with acid potassium fluoride to decompose the ore. The resulting melt was solubilized in hot water and acidified with hydrofluoric acid. This produced a mixture of potassium zirconium fluoride and potassium hafnium fluoride in solution and led to the first successful separation of hafnium from zirconium by fractional crystallization.

A similar fusion is employed by Kawecki as a part of his process to produce potassium zirconium fluoride. According to patents [27, 28] held by him, the reactions are essentially



and



The Kawecki process is employed also by the Russians [29] in the preparation of pure zirconium oxide from zircon. In their procedure the ore is first ground to 200 mesh and mixed with potassium silico fluoride and potassium chloride. It is said that the potassium chloride promotes complete decomposition of the zircon.

This mixture is then heated at 650–700° C in a rotary kiln to produce rounded off and slightly fused granules having an average size of 0.5–10 mm. The nodules containing 13–14 percent zirconium,

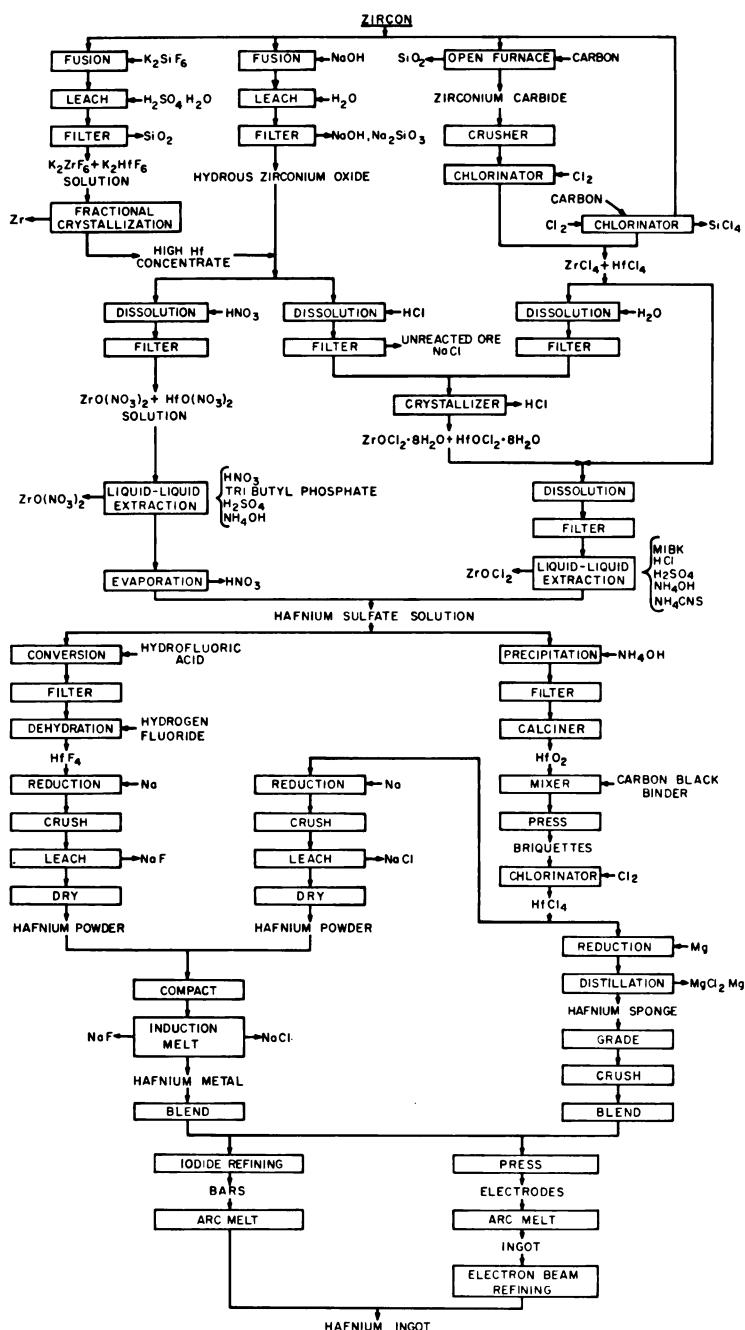


FIGURE 2.1. Flowsheet for the Production of Hafnium from Zircon.

the equivalent of 40–43 percent $K_2 ZrF_6$, are crushed and leached in a 1 percent hydrochloric acid solution.

The potassium fluozirconate solution thus formed becomes the feed material for further processing and separation of hafnium from zirconium by crystallization as described in a later section of this chapter.

A third type of fusion employs caustic soda as the cracking agent. This process reportedly has been adopted by Columbia-National Corporation in their new zirconium production plant.

Pilot plant work accomplished at Iowa State College [30] and the Bureau of Mines [31] demonstrated the feasibility of this process. These workers were in good agreement concerning ratio of caustic to sand, reaction time, reagent consumption, and an over-all cost of about 50 cents per pound of contained zirconium in the product.

Caustic soda and zircon are mixed in about equal proportions by weight and charged in mild steel pots to furnaces which are held at a temperature of 600–650° C for from 1–2 hours. A spongy mass or frit formed during the reaction is dissolved in hot water. Separation of the water soluble silicates from the insoluble zirconate is accomplished in a continuous centrifuge. Finally, the insoluble zirconate is dissolved in acid and recrystallized to improve purity.

Figure 2.2 shows the general layout of a plant to produce zirconyl chloride for feed to a hafnium separation plant using the hexonethiocyanate system. Substitution of nitric acid for hydrochloric acid results in the production of zirconyl nitrate which is more suitable for feed material to a separation plant employing the tributyl phosphate-nitric acid system.

A fusion employing sodium carbonate is described in a patent by William R. Loveman [32]. Finely divided ore is mixed in the ratio of one part to eight parts of sodium carbonate. The mixture is fused at 1,000° C for about 2 hours. When the reaction is complete and the fused mass has cooled, it is placed in a suitable vessel with water and sparged with steam. Impurities such as aluminum and silicon are leached away as sodium aluminate and sodium silicate leaving the insoluble salts sodium zirconate, sodium titanate, and ferric hydroxide. Subsequently, a weak acid leach dissolves the titanium and iron salts leaving a reasonably pure zirconium hydroxide which would be suitable as feed to the hafnium-zirconium separation system.

Carbothermic Reaction

To the present, virtually all metal production has been accomplished via the carbide-chlorination route. The basic operation differs only in the type of electric furnace and chlorinators employed.

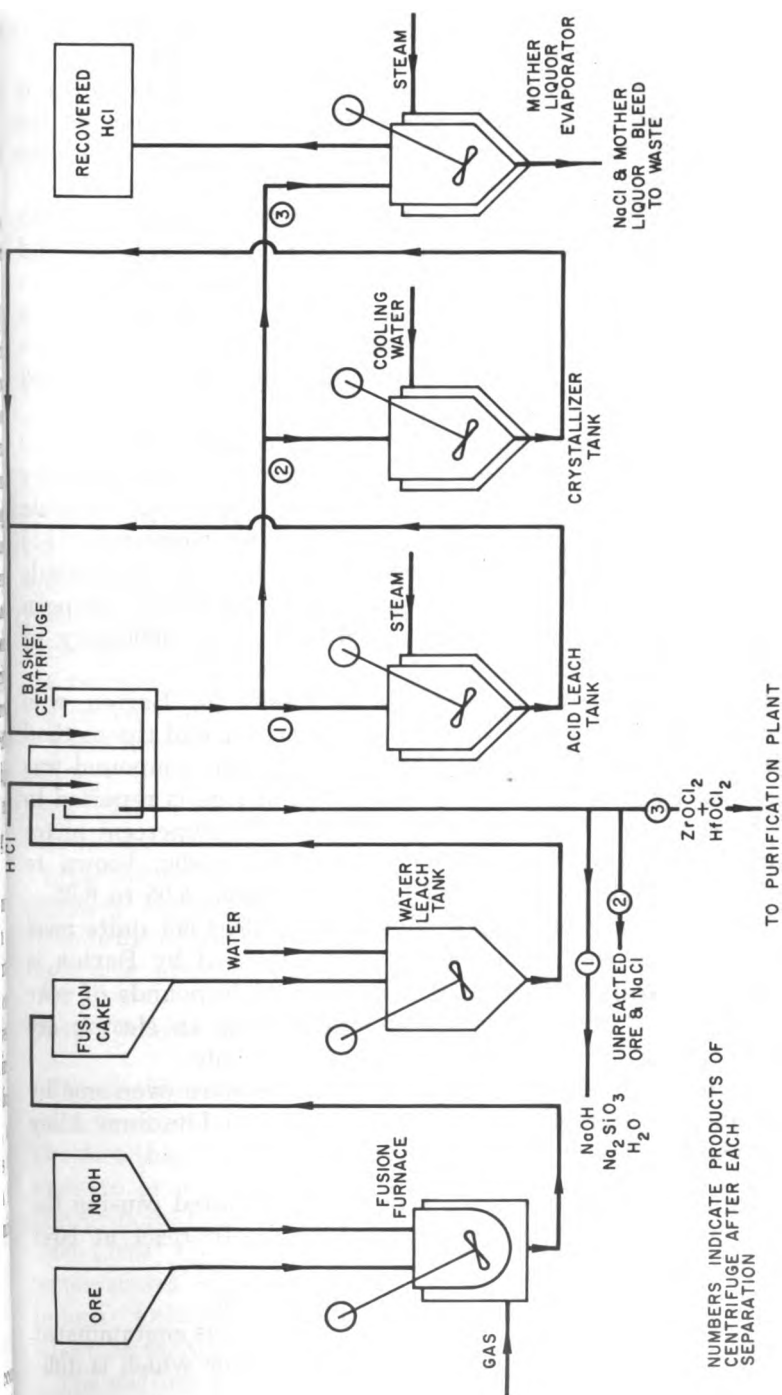


Figure 2.2. Plant Layout for Recovery of Zirconium-Hafnium from Ore by Caustic Soda Fusion.

Zircon and graphite (or coke) is mixed in a ratio of, roughly, 4:1 and charged in small increments to an arc furnace. The zirconium-to-silica bond is broken freeing silicon monoxide which is evolved from the reaction zone and burns to the dioxide at the mouth of the furnace. The zirconium oxide is converted to the carbide which forms a fused block or ingot under the electrode.

Upon completion of a batch, the carbide ingot is smothered with unreacted charge, graphite, or charcoal to prevent oxidation and allowed to cool. Since unreacted charge is generally employed to serve as a refractory wall during the reaction, it is necessary to separate the product by screening. The unreacted charge is then returned to the furnace and the carbide crushed and sized for feed to the chlorinator.

The product of the carbide furnace has a golden yellow-bronze color tinged with blue to violet. It is also known in the industry as carbonitride (The Carborundum Corporation) and cyanonitride (Titanium Alloys Mfg. Co.). These are not true compounds [33] as the nomenclature implies but more nearly trade names for carbide having varying amounts of nitrogen present. Actually nitrogen combines in larger quantities only when there is a deficiency of carbon in the charge.

The term cyanonitride was coined by Louis E. Barton who disclosed this new and useful composition of matter and the method of producing it in his patent [34, 35]. Actually, the compound was produced first by Renoin [36] in 1900. Cyanonitride is reported to contain 82-84 zirconium, 3-5 percent carbon, and 8-10 percent nitrogen; to have a metallic luster; to be, usually, golden brown to bronze in color; and have a specific gravity of about 5.95 to 6.35.

While the cyanonitride being produced today does not quite meet these specifications, the method and charge described by Barton is employed successfully. His charge, consisting of 20 pounds of coke and 100 pounds of zircon, was added gradually to an electric arc furnace at temperature such as to decompose the oxide.

Some of the disadvantages of Barton's process were overcome by Kinzie *et al.* in a later patent [37] also assigned to Titanium Alloy Manufacturing Company. These are as follows:

- (a) The intense heat of the arc is higher than required causing the formation of hard lumps which are difficult to react at later periods.
- (b) Explosions occur as a result in part due to (a).
- (c) The product formed is not pure cyanonitride but is contaminated with considerable quantities of zirconium carbide which is difficult to crush and burn to the oxide.

Such disadvantages are overcome by use of an intermittent charging practice and by blowing air through an upper passage of electrode into the reacting mass. The charge described by Kinzie consists of 62.5 parts of zircon sand, 13.3 parts of high carbon coke, and 24.2 parts of refuse (recycle of unreacted charge). Every 10 minutes, 15 pounds of mixture is shoveled in until the furnace is full, and the upper electrode is raised to secure a suitable arc each time material is shoveled in. The current input is adjusted at 15,000 amperes and 50 volts and the air input adjusted to 6 cubic feet per minute.

The Bureau of Mines [38, 39] employed a single-phase furnace having one retractable electrode above a graphite, water-cooled base through which a current of approximately 2,500 amperes at 100 volts was passed. The furnace crucible consisted of plates of graphite standing on end and forming an hexagonal tube. Charcoal was packed between this tube and the silicon carbide, rammed lining of the shell. The furnace was fed by hand scoop through a side opening as required. A second opening in the upper furnace shell permitted observation of the reaction and enabled the operator to raise, lower, or swing the electrode and obtain complete reaction of the batch. A third opening was attached to a duct through which the rather copious silica fumes were withdrawn.

The Carborundum Metals Company at their Niagara Falls plant employs a single-phase arc furnace having two carbon electrodes suspended in an unlined, cast steel crucible. A mix of zircon and coke breeze is charged to the furnace and reacted to form the carbide. Unreacted mix around the reaction zone protects the steel shell from excessive heating. A batch of 3,000 pounds is produced per run. It is believed that Carborundum will use a three-phase furnace in their new plant at Parkersburg, West Virginia.

Direct Chlorination of the Ore

Direct chlorination of zircon would at first glance appear to be the most direct and best approach to the production of the tetrachloride. The fact that no producer in the United States employs this method seems to be a good indication that it is not an economical process. The principal disadvantage of the method is the high temperature (800–1,000° C) required to promote a reasonable reaction rate. At temperatures such as these chlorine is very corrosive on furnace linings. Other disadvantages consist of the high chlorine wastage to silicon tetrachloride and the fineness (–200 mesh) of grind required.

The method was used by I. G. Farbenindustrie [40] at the Leverkusen Works during World War II. The method was originally

developed to chlorinate baddeleyite with a mixture of carbon monoxide and chlorine. The reaction of the ore with the chlorinating agent was incomplete leaving almost one-third of the ore as residue. This was believed to be caused by the low temperatures of 500–600° C in the chlorinator.

In 1943, when shipments of baddeleyite into Germany were curtailed, it became necessary to substitute zircon sand. This was found to be impossible to chlorinate at temperatures as low as 600° C. A new procedure was evolved that required an excess of carbon in the charge and an excess of oxygen to elevate the temperature to 800–1,000° C. In addition, a mix consisting of 330 pounds of zircon, 132–165 pounds of powdered coal, and 5.3 gallons of concentrated sulphite liquor was briquetted, coked, and charged to the chlorinator at temperatures ranging from 800 to 1,000° C. A mixture consisting of 350–530 cubic feet (STP) chlorine gas and about 170 cubic feet of oxygen was charged each hour.

The capacity of the chlorinator was 660–880 pounds of zirconium tetrachloride per day, or about 3.7 pounds of tetrachloride per square foot of bed area per hour, with an operating time of 80 percent. Recovery of zirconium amounted to 65 percent. Chlorine recovery in zirconium tetrachloride was 60 percent.

Chlorination of the Carbide

Chlorination of the carbide is accomplished in a variety of different types of equipment. In the simplest process the carbide is charged to a vertical tube having a charging port and a side arm outlet at the top and a flat or cone bottom pierced with chlorine inlets. The initial charge is heated to promote chlorination which then continues without external heating on introduction of chlorine gas. The chlorine passes through and reacts with the charge to produce a crude hafnium-zirconium tetrachloride. This is collected in a cone-bottom condenser and discharged periodically into containers.

The apparatus is ordinarily of simple mild steel construction and is cooled with copious quantities of water to minimize corrosion.

The carbide chlorinates readily at 500° C. The chlorination temperature is held in check by limiting and adjusting the chlorine flow. A simple shaft-type chlorinator produces approximately 25 pounds of tetrachloride per square foot per hour with yields as high as 95 percent.

2.4 SEPARATION OF HAFNIUM AND ZIRCONIUM

By R. H. Nielsen ¹

Although many early researchers claimed to have found traces of element 72 in zirconium or rare-earth ores, these claims were never substantiated. The Bohr atomic theory was the basis for postulating that element 72 should be tetravalent rather than trivalent. Subsequently, following a suggestion by Bohr, Coster and de Hevesy examined the X-ray spectra of several zirconium concentrates. They found lines at the positions and with the relative intensities postulated by the Bohr theory [41, 42].

This discovery then marked the beginning of the search for a suitable method of separating hafnium from zirconium. Of the many processes developed, most fall into a classical grouping of academic interest only. The metal-producing processes of economic importance today include only liquid-liquid extraction and crystallization. Table 2.6 lists the various hafnium-zirconium producers and their separation method. Other major operations in the production process are also shown and identified where known.

Liquid-Liquid Extraction

The hexone-thiocyanate separation process was developed by Union Carbide and Carbon Chemicals Division at their Y-12 plant in Oak Ridge, Tenn. This process, with variations, is employed in the United States by Wah Chang Corp., Carborundum Metals Corp., and Mallory Sharon Metals Corp. In 1958 these companies produced a total of 2,000,000 pounds of zirconium and 21,400 pounds of hafnium sponge. These plants have a planned capacity in excess of 5,000,000 pounds of zirconium and the equivalent of 100,000 pounds of hafnium.

The tributyl phosphate-nitric acid separation system, a product of the laboratories at Iowa State College, is employed by the Columbia-National Co. in a plant with capacity to produce approximately 1,000,000 pounds of zirconium and the equivalent of 20,000 pounds of hafnium. It is believed that the French will employ this system also when production is commenced. A comparison of costs prepared by J. M. Googin [43] indicates that the tributyl phosphate system may be the more economical of the two production methods.

¹ Wah Chang Corp.

TABLE 2.6—HAFNIUM-ZIRCONIUM PRODUCERS

| Company | Ore | Conversion | Separation | Reduction |
|---------------------------------------|--------------------|--|-----------------------------------|----------------|
| UNITED STATES | | | | |
| Wah Chang----- | Australian Zircon. | Carbide-Chlor. | MIBK-HCNS | Kroll—Mg. |
| Carborundum----- | Florida Zircon. | Carbide-Chlor. | MIBK-HCNS | Kroll—Mg. |
| Columbia-National. | Florida Zircon. | Caustic Fusion. | TBP-HNO ₃ | Kroll—Mg. |
| Mallory Sharon---- | Florida Zircon. | Carbide-Chlor. | MIBK-HCNS | Mod. Kroll—Na. |
| FRANCE | | | | |
| Thann et Mulhouse Bozel-Nobel Planet. | ----- | Chlor. | TBP-HNO ₃ | Kroll—Mg. |
| GERMANY | | | | |
| Degussa----- | ----- | Carbide-Chlor. | MIBK-HCNS | Mod. Kroll—Mg. |
| GREAT BRITAIN | | | | |
| Magnesium Elektron. | ----- | Caustic Fusion | MIBK-HCNS | Kroll—Mg. |
| JAPAN | | | | |
| Toyo----- | ----- | Carbide-Chlor. | MIBK-HCNS | Kroll—Mg. |
| RUSSIA----- | ----- | K ₂ SiF ₆ Fusion | Crystallization (plus MIBK-HCNS). | ----- |

The product of the above separation systems is the oxide. The manufacturing processes followed to produce the oxide are described in the first part of the following section, and the less used, classical separation methods are described later.

The Hexcone-Thiocyanate Separation System

The thiocyanate extraction process was discovered by Fischer and Chalybaeus [44, 45], who extracted the hafnium thiocyanate complex from a sulfate solution into diethyl ether. In six months of extensive development [46-57], Union Carbide and Carbon Chemicals Division converted this information into an operating plant capable of producing 40,000 pounds of zirconium oxide per month. In the commercial process, the hafnium thiocyanate complex is preferentially extracted into methyl isobutyl ketone (hexone) from a hydrochloric-thiocyanic acid solution.

It is interesting to note that Fischer [44] first used a hydrochloric acid system for the thiocyanate separation, but changed to sulfuric

acid because of the resulting higher separation factor. During the development at Oak Ridge, sulfuric acid was replaced with hydrochloric acid, even with a decrease in separation efficiency, because the chloride system would allow a four-fold increase in metal concentration in the aqueous solution. This greatly increased the capacity of the separation plant.

Feed solution for the hexone-thiocyanate system is usually prepared by carefully dissolving the mixed hafnium-zirconium tetrachlorides in water and adding ammonium thiocyanate. Zirconyl chloride can also be used, however (see Fig. 2.1). The final feed solution

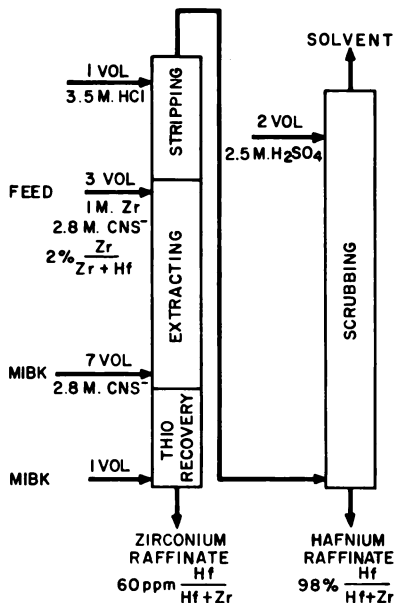


FIGURE 2.3. MIBK-HCNS Extraction System.

containing 1.3 molar metal content, 2.8 molar ammonium thiocyanate, and 1 normal free acid is extracted with methyl isobutyl ketone containing 2.8 molar thiocyanic acid as indicated in Figure 2.3.

Various types of contactors are being used for this extraction, including open spray columns, baffled spray columns, perforated-plate pulse columns, and mixer-settlers. The system installed by the U.S. Bureau of Mines in 1952 consisted of open spray columns using long vertical sections of 4-inch diameter glass pipe. This included 50 feet for thiocyanate recovery, 200 feet for extraction, 150 feet for stripping, and 50 feet for sulfuric acid scrubbing.

Hafnium is extracted preferentially as the thiocyanate complex by the solvent and carried into the stripping system where 3.5 molar hydrochloric acid strips and returns zirconium to the extraction columns. Both low acid and high thiocyanate concentrations in the

aqueous feed promote the extraction of metal into the solvent phase. High acid and low thiocyanate concentration favor stripping of metal from the solvent. Hafnium-laden solvent leaving the stripping columns enters the scrubbing column and passes countercurrent to 5 normal sulfuric acid. Hafnium and other metallic ions such as boron and titanium are scrubbed into the sulfuric acid solution and carried into the hafnium product storage tanks.

The hafnium sulfate solution is mixed with ammonium hydroxide to precipitate hafnium as the hydrous oxide. When high purity hafnium is not required, the hydrous oxide is then filtered, washed, and charged into a rotary kiln where the cake is dried and calcined to the oxide.

If high purity hafnium is required the hydrous oxide cake is repulped in hydrochloric acid and reprecipitated as hafnium phthalate. Conditions for the precipitation are given in Table 2.7.

TABLE 2.7—CONDITIONS FOR PHTHALATE PRECIPITATION OF HAFNIUM

| | |
|------------------------------------|-----------|
| Metal concentration (lb/gal) | 0. 1-0. 3 |
| Temperature (°F) | 190 |
| pH | 1. 5 |

The hafnium phthalate filter cake is then repulped with ammonium hydroxide to form hafnium hydroxide and ammonium phthalate which is returned to the system. The hafnium hydroxide is then dried and calcined to the oxide. A very detailed and complete description of the entire separation process is contained in the *Reactor Handbook* [58].

TBP-Nitric Acid System

The first work using tributyl phosphate (TBP) as a solvent to extract zirconium from hafnium was reported by Kerrigan *et al.* [59, 60]. Zirconium was extracted from an aqueous solution containing 0.55 M ZrOCl_2 , 1.64 M CaCl_2 , 0.6 M HCl , and 2.88 M HNO_3 by an equal volume of solvent consisting of 60 percent TBP-40 percent dibutyl ether, containing 2.13 M HNO_3 . The subsequent process development and modification [61-64] by Beyer, Cox, and Peterson at Iowa State College led to its commercial use by the Columbia-National Corporation [65]. Parallel studies in Europe [66-68] resulted in a similar process [69, 70] differing in concentration and in the particular TBP diluent used.

Preparation of the feed solution can be accomplished by several methods such as: (1) caustic fusion of zircon, followed by washing, sulfuric acid dehydration, hydroxide precipitation, and dissolution in nitric acid [64]; or (2) dissolution and dehydration of calcium

zirconate with sulfuric acid, then hydroxide precipitation and dissolution in nitric acid; or (3) dissolution of zirconium tetrachloride followed by hydroxide precipitation and nitric acid dissolution. The critical point of the first two methods is the reduction of silica and sulfates to a sufficiently low concentration to eliminate the formation of silica gel or insoluble basic sulfates during the extraction.

In the extraction, the distribution coefficients of both zirconium and hafnium vary directly with the acid concentration of the system. The coefficient for zirconium usually is much greater than one, while the coefficient for hafnium is usually less than one. However, the separation factor decreases with increasing acid concentration.

Pure TBP results in greater distribution coefficients and larger separation factors, but dilution with an inert hydrocarbon solvent is necessary to reduce the viscosity and density of the solvent phase.

The optimum separation flow conditions [65] are shown in Figure 2.4. One volume of feed solution containing 1 M zirconium plus hafnium as nitrates and 8 M free HNO_3 is extracted with 3.6 volumes of 50–50 TBP-n-Hexane previously equilibrated with 8 M HNO_3 . Hafnium and impurities are back-scrubbed with 0.7 volume of 5 M HNO_3 and leave the contactor in the aqueous stream. The solvent extract containing zirconium is stripped with 0.9 volume of deionized water in a second contactor to remove the zirconium. Both metal product streams can be distilled to recover the nitric acid values, then neutralized to precipitate each hydrous oxide.

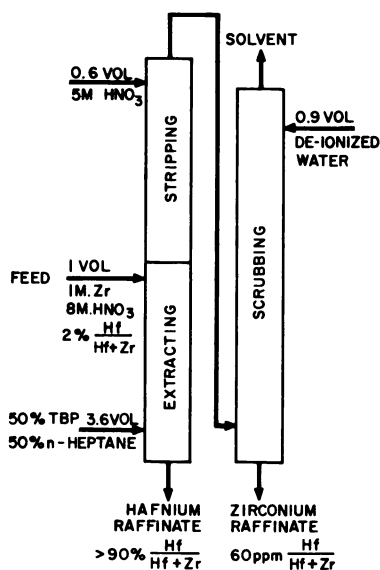


FIGURE 2.4. TBP- HNO_3 Extraction System.

The zirconium oxide product is free of most impurities because these remain in the nitric acid solution with the hafnium.

While the above conditions will undoubtedly yield hafnium with a low zirconium content, the only available data concerning the use of the TBP-nitric acid system to produce high purity hafnium oxide were presented by Foos and Wilhelm [71]. Hafnium tetrachloride containing about 3 percent zirconium tetrachloride was hydrolyzed in water and crystallized as oxychlorides for feed. The selected extraction conditions were (a) an aqueous feed of 5.8 M nitric acid containing dissolved oxychlorides equivalent to 280 g of oxide per liter, (b) a solvent phase of 40 percent dibutyl ether and 60 percent TBP, and (c) an aqueous scrub solution of 5.8 M nitric acid. The flow ratios were 4:4:1, respectively. The contactor had 11 physical stages of extraction and 6 stages of back scrubbing. The aqueous raffinate contained 86 percent of the input oxides, and the zirconium content of the hafnium was less than 20 ppm. Over 100 pounds of high purity hafnium oxide were produced by this procedure.

During the above operation, chloride ion measurements led Foos and Wilhelm to conclude that the extracted species did not possess a chloride atom. This would indicate that the nitrate form is preferentially extracted from a mixed acid solution, because Levitt and Freund [72] have extracted zirconium as a chloride-TBP complex from a hydrochloric acid solution.

In a recent study [73] on the extraction of hafnium and zirconium from a sulfuric acid solution, 10 percent of the combined metals were extracted in one contact, but no separation occurred. With thiocyanate ions added to the sulfate solution, a separation factor of 4 was obtained. In this method, contrary to the results obtained with nitric acid, hafnium is preferentially extracted.

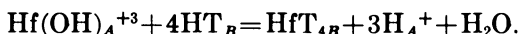
Diketones

Following the work of Connick and McVey [74] in using thenoyltrifluoroacetone (TTA) to extract zirconium into benzene, TTA and other diketones were investigated as selective extracting agents for the separation of zirconium and hafnium. However, the systems have very slow reaction times, the diketones are expensive, and the solutions are very dilute. Therefore, in comparison with other liquid-liquid extraction systems, these systems are primarily of academic interest in studying reaction mechanisms and the formation of complexes.

Huffman and Beaufait [75], using a solvent of 0.025 M TTA in benzene, extracted a 2 M perchloric acid solution containing 0.24 g of metal (62 percent hafnium) per liter. Two equal volume ex-

tractions yielded 27 percent of the original hafnium in the aqueous phase with a content of less than 1.2 percent zirconium. A patent [76] has been issued for the process.

The extraction of hafnium from nitric acid was studied by McCarty, Dearing, and Flagg [77] who showed that the extraction is a varying function of the acid concentration and also of the TTA concentration. Hafnium and zirconium differed markedly in the time required to reach equilibrium, hafnium taking 80 to 90 minutes while the zirconium equilibrium was essentially complete after 10 minutes. Comparable studies by McBride [78] on hafnium extraction indicated that the extraction has a third-power dependence on hydrogen ion concentration and a fourth-power dependence on TTA concentration. All extractions were equilibrated for 2½ hours. The reaction proposed was



Schultz and Larsen [79] studied the variables involved in extracting zirconium and hafnium from a 0.2 N hydrochloric acid solution with a benzene solution of trifluoroacetylacetone. The extraction coefficients appeared to follow a fourth-power dependence on the diketone activity at constant hydrochloric acid concentration and constant initial metal ion concentration. Some indications of chloride complexing were found, with the hafnium-chloride complex stronger than the zirconium-chloride complex.

In the purification of zirconium it was desirable to remove zirconium with the least amount of hafnium; therefore, low diketone concentrations were used. Using benzene containing 0.0375 M trifluoroacetylacetone, two extractions produced zirconium with less than 0.2 percent from an initial 2.9 percent hafnium mixture, with a yield of 7 percent. Similarly, in the purification of hafnium it was desirable to remove the major constituent, zirconium, with the least number of extractions. This was accomplished by using a higher diketone concentration. Using benzene containing 0.075 M trifluoroacetone, 99.94 percent hafnium was obtained in six extractions with a 37.6 percent yield from an initial mixture containing 13.7 percent hafnium.

Larsen and Terry [80] made a comparison of some diketones which could be used for the separation of zirconium and hafnium. The aqueous solutions were 2 M perchloric acid, except when trying trifluoroacetylacetone for which 0.5 M perchloric acid was used. The equilibrium metal concentrations were 0.003 M or less. The benzene phase contained 0.075 M diketone. In general, the diketones could be placed in two categories: those containing the CF_3 group which gave a measurable extraction of the metals into the benzene

was recommended [87] because their greater solubility facilitated the handling of larger amounts of the salts (see Table 2.11). Crystallization was accomplished by cooling a hot concentrated solution. Although a 99 percent hafnium product was obtained in 48 crystallizations, over 650 crystallizations were performed to extract, in a concentrated form, the major part of the hafnium present in the original ore.

In 1949 and 1950, the Brush Beryllium Company did considerable development work on fluoride crystallization methods [88]. Although their preliminary work gave very good separations using the crystallization of potassium double fluoride salts, most of their work was done with the ammonium double fluorides for reasons similar to those of de Hevesy. The crystallizations were hampered by formation of the more stable ammonium zirconium heptafluorides and zirconium oxides by hydrolysis, especially in the vacuum evaporators. Hydrolysis was limited by keeping the solution at a pH of 1 to 2 with the addition of hydrofluoric acid. During the course of this work it was found that the presence of fluosilicic acid materially enhanced the separation, reducing by a factor of three the number of crystallizations required to achieve a particular level of hafnium in the zirconium.

TABLE 2.11—SOLUBILITY OF FLUOZIRCONATES IN WATER [88]

| Temp (° C) | Solubility (g/liter H ₂ O) | | |
|------------|---------------------------------------|--|--|
| | K ₂ ZrF ₆ | (NH ₄) ₂ ZrF ₆ | (NH ₄) ₂ ZrF ₆ |
| 20----- | 19.8 | 273 | 244 |
| 40----- | ----- | 353 | 253 |
| 50----- | ----- | 400 | 321 |
| 60----- | 96 | 565 | 384 |
| 80----- | ----- | 722 | 461 |
| 100----- | 305 | ----- | 559 |

The industrial use of the potassium fluozirconate crystallization to produce hafnium-free zirconium has been described [29, 89] and has been used by the Kawecki Chemical Co. The production rate of the Russian operation is not known but is believed to be in excess of 1,000,000 pounds of zirconium per year. A comparison of the data on hafnium separation is shown in Figure 2.5. No recovery data were available. This process is not recommended [90] for the production of zirconium-free hafnium, however, because of interference from impurities and hydrolysis products which accumulate in the liquid phase. Unconfirmed information indicates that the Russian practice has been to transform the high-hafnium concentrates into a feed for the hexone-thiocyanate extraction system.

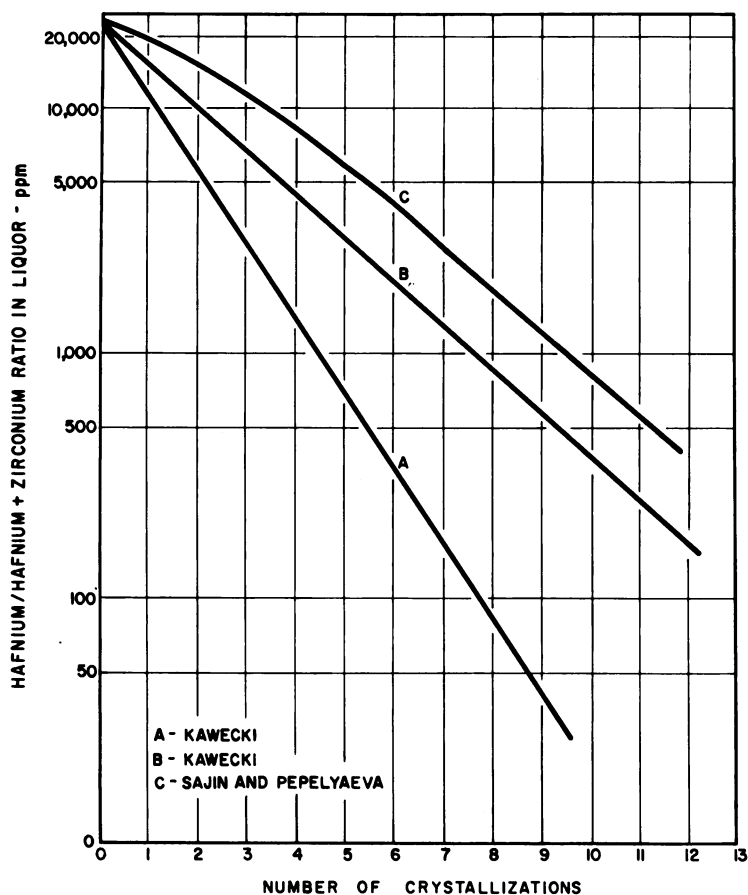


FIGURE 2.5. Comparison of Data on Hafnium Separation.

Oxyhalides

The differences in solubility of hafnium and zirconium in halogen acids are low and not generally used as a means of separation. However, the crystallization of the oxychlorides in concentrated hydrochloric acid has been recommended for the final purification of hafnium produced by crystallization of the potassium double fluoride salts [91]. The solubilities of the corresponding oxyhalide salts in strong halogen acids are shown in Table 2.12.

TABLE 2.12—SOLUBILITY OF OXYHALIDES IN HALOGEN ACID SOLUTIONS AT 20° C

| Acid | Normality | $HfOX_2$ | $ZrOX_2$ | Reference |
|----------|-----------|----------|----------|-----------|
| HCl----- | 6.35 | 0.1030 | 0.1037 | 92 |
| | 11.61 | 0.1509 | 0.334 | 92 |
| | 12 | 0.090 | 0.310 | 93 |
| HBr----- | 13 | 0.0038 | 0.0172 | 94 |
| HF----- | 20 | 1.22 | 2.34 | 94 |

Other

Drophy and Davey [95] suggested using the citrate salts for separation because hafnium citrate is supposedly more soluble than zirconium citrate. Attempts to separate the citrate salts have not resulted in measurable separations [96]. Ammonium and potassium double oxalates [97] can be crystallized to separate zirconium and hafnium. Hafnium concentrates in the mother liquor. Ammonium and potassium double sulfates of zirconium and hafnium can be separated similarly by crystallization [98, 99]. De Hevesy and Logstrup [100] investigated the solubilities of acetylacetone derivatives of hafnium and zirconium in various solvents. At 25° C in ethylene bromide, the hafnium salt solubility is 0.620 mole per liter, and the zirconium salt solubility is 0.0907 mole per liter.

Ion Exchange .*Cation Resin Exchange*

Street and Seaborg [101] first discovered the cation separation of zirconium and hafnium. Dowex-50 resin was slurried in a 2 M perchloric acid solution containing 0.01 M zirconium plus hafnium (30 percent hafnium oxide) as oxychlorides. The resin slurry was placed on top of a Dowex-50 column and eluted with 6 M hydrochloric acid. Hafnium was eluted first. Street and Seaborg obtained 66 percent (10 mg) of the starting hafnium oxide containing only 0.1 percent zirconium oxide. Cooper and Dinzey [102], after using the same procedure with 2.3 g of mixed oxides containing 3.6 percent hafnium oxide, concluded that "The method is better suited to the production of hafnium-free zirconium than of hafnium uncontaminated by zirconium." Newnham [103] similarly treated 2 g of oxides containing 20 percent hafnium oxide and recovered a first fraction containing 42 percent of the starting hafnium oxide, 99.9 percent pure.

Using a similar charging procedure, Lister [104] investigated the elution characteristics of sulfuric, hydrochloric, nitric, perchloric, and oxalic acids. Sulfuric acid, which preferentially removed zirconium, was selected as the most effective eluant for the separation. In addition, zirconium loading of the resin was found to be more efficient with nitric acid rather than perchloric acid. Among the other eluants, 3 N hydrochloric acid gave a better separation than 6 N hydrochloric acid, but not complete. The first effluent oxide was 34 percent hafnium, and the zirconium product contained 0.14 percent hafnium. Tests with 0.01 and 0.001 M oxalic acid resulted in very rapid elution and poor separation. Analysis indicated that zirconium is eluted first by oxalic acid. Nitric acid, 3 N, eluted at

a rate very similar to that of hydrochloric acid but with no separation. Perchloric acid, which forms only weak complexes with zirconium, gave a very slow elution with no separation.

Lister's revised procedure [105] was to load the column, which was 2.5 cm in diameter, 120 cm long, and held 350 g of 0.5 mm diameter Zeocarb 225 resin (very similar to Dowex-50), by slowly passing through the column 1 liter of 2 N nitric acid containing 20 g of zirconyl nitrate. The absorbed material was eluted with 1 N sulfuric acid at a flow rate of 100 ml/hr. The first 9 liters contained 95–98 percent of the zirconium with less than 0.01 percent hafnium. Lower sulfuric acid concentrations (0.8 N) gave better separations, but longer elutions were necessary. After the zirconium has eluted, the hafnium may be quickly eluted with 3 N sulfuric acid or oxalic acid. Subsequent work [106] with a 75 percent hafnium starting material, treated in a similar manner, produced a hafnium product containing only 0.3 percent zirconium.

Benedict, Schumb, and Coryell [107] made a very complete survey of the effects of varying concentrations of sulfuric, hydrochloric, and nitric acids. Graphs are presented showing the percent absorption of hafnium and zirconium by Dowex-50 resin from 0.2 to 11.5 M hydrochloric acid, 0.5 to 14.8 M nitric acid, and 0.39 to 4.7 M sulfuric acid. The best separation using only mineral acids was with 0.39 M sulfuric acid, which confirmed the work of Lister, but much better separations occurred when citric acid was added to nitric acid solution as a complexing agent. An eluant of 0.45 M nitric-0.091 M citric acid preferentially removed zirconium from a Dowex-50 column with a 99 percent recovery substantially free of hafnium. All of the work was done with radioactive tracers in very dilute solutions.

Larsen and Wang [108], in studying the ionic species of zirconium and hafnium in perchloric acid, found that zirconium is preferentially absorbed by Amberlite IR-120.

In all of the cation exchange studies, small amounts of both zirconium and hafnium are present in the first column effluents. Apparently a small fraction of the metals is present in a colloidal or polymerized condition such that the metals are not absorbed or delayed by the resins.

Anion Resin Exchange

Kraus and Moore [109] eluted tracer quantities of Zr-95 and Hf-181 through a 107-cm column of Dowex-1. The column was 0.0226 sq cm in cross section, and the 0.5 M hydrofluoric-1.0 M hydrochloric acid solution flow rate was 0.3 ml/sq cm/min. Zirconium was eluted first, and the hafnium content of the last fractions was greater than 95 percent. In studying the effects of varying concentration, Kraus and Moore [110] showed that the elution rate for

zirconium was about proportional to the square of the hydrochloric acid concentration and independent of the hydrofluoric acid concentration.

Huffman and Lilly [111] dissolved 20 mg of zirconium and 10 mg of hafnium in 10 ml of 0.32 M hydrofluoric acid. Ninety-six percent of the metal was absorbed by 600 mg of Amberlite IRA-400 resin, which was washed with water and transferred to the top of a column of the same resin 30 cm long and 0.78 sq cm in cross section. Elution with a 0.2 M hydrochloric-0.01 M hydrofluoric acid mixture was conducted at the rate of 6 ml/hr. The first 69 percent of the zirconium contained no detectable hafnium. The last fraction, containing 83 percent of the hafnium, contained 0.03 percent zirconium.

In further work, Huffman and Lilly [112] sought to explain the elution rates as functions of eluant composition. Reduced hydrochloric acid concentration reduces the elution rate, broadens the individual metal peaks, and spreads the peaks apart. Forsling [113], eluting with 0.22 M hydrochloric acid and 0.00002 to 0.02 M hydrofluoric acid, found no essential change in the separation as a result of changing the hydrofluoric acid concentration.

Anion exchange of the chloro complexes of zirconium and hafnium was demonstrated by Huffman, Iddings, and Lilly [114]. Zirconium and hafnium, in quantities of 3.8 g each, were absorbed slowly at the top of the column. The absorbed metals were eluted, hafnium first, from the Dowex-2 resin with 9 M hydrochloric acid at a rate of 10–12 ml/hr. The lucite column was 11 cm long and 6.5 mm ID.

Rajan and Gupta [115] eluted hafnium from Amberlite IRA-400 with 1 N H_2SO_4 . A 3–4 g quantity of resin was equilibrated with a stock solution containing 4–4.5 g of potassium double fluorides in 2 liters of water. The saturated resin was placed on top of columns 55 cm long and 2.2 cm in diameter with the resin in a chloride or sulfate form. The bed was eluted with 1 N H_2SO_4 until the oxides in the effluent diminished; then the eluting concentration was gradually raised to 2 N. About 90 percent of the zirconium oxide was recovered free of hafnium.

Adsorption

The selective adsorption of hafnium compounds by activated silica gel was first reported by Hansen and Gunnar [116, 117]. A 1:5 solution of zirconium-hafnium tetrachlorides in methanol was slowly passed through a 30-inch column of silica gel which had been activated at 300° C for 4 hours. The first effluent was essentially free of hafnium. The adsorbed hafnium-zirconium compounds were stripped from the silica gel using methanol containing 1.2 M anhydrous hydrogen chloride.

Subsequent developments [118] showed that methanol was a better solvent than acetone, acetic acid, water, ethanol, or isopropanol. Acetone solutions gave good preferential adsorption of hafnium, but tarry decomposition products were also formed. No other ketones were tested. The column capacity was limited by the product purity. Using the normal 2 percent hafnium-zirconium tetrachloride, a product containing less than 100 ppm hafnium could be obtained if the feed were limited to 1 pound of entering tetrachloride to each 10 pounds of SiO_2 . For columns filled with 28–200 mesh silica gel, a flow rate of 20 cm/hr based on an empty column was recommended.

Most of the adsorbed zirconium could be preferentially stripped from the column with methanol. A subsequent stripping with methanol containing 2.5 M anhydrous hydrogen chloride will remove both zirconium and hafnium from the column, with the hafnium concentrated to 37 percent in the stripped product. An aqueous 7 N sulfuric acid solution will remove all traces of both metals from the column.

The equilibrium constants [119] for the solvolysis of the tetrachlorides in methanol and ethanol indicate more extensive solvolysis occurs in methanol, with hafnium tetrachloride reacting more than zirconium tetrachloride. It would appear that these equilibria were the limiting factors in the selective adsorption.

The zirconium can be recovered by distillation of the methanol for reuse. The residues are taken up in hydrochloric acid and recrystallized as the oxychloride to remove common impurities such as aluminum, iron, and titanium. No attempts were made to convert the distillation residues directly to tetrachlorides.

Further development of this process included operation of a continuous countercurrent pilot plant column [120] and a subsequent economic evaluation [121], which was not favorable compared with the hexonethiocyanate process.

Distillation

Phosphorous Oxychloride Complex

Van Arkel and de Boer [122] first published a procedure for separation of the two elements by what they termed a fractional sublimation of the complexes formed by zirconium-hafnium tetrachlorides with phosphorous pentachloride. The freezing point and boiling point for the zirconium complex were given as 164.5°C and 416°C , respectively. They also prepared the phosphorous oxychloride complexes with boiling points of about 360°C .

A detailed investigation [123] of vapor pressures of the pure oxychloride complex resulted in boiling point determinations of 360°C and 355°C for the zirconium and hafnium compounds, re-

spectively. The ratio of the volatilities at the boiling points is 1.14. The heat of vaporization for both complexes is 20.5 ± 0.5 Kcal.

An experimental distillation in a glass Oldershaw column containing 50 physical plates with a feed of 2.5 percent hafnium/zirconium produced a first overhead fraction (5 percent) containing 16 percent hafnium/zirconium. After distilling away 40 percent of the charge, the residue contained less than 0.2 hafnium/zirconium.

Williams *et al.* [124, 125] attempted to produce low-hafnium zirconium in a pilot plant built of Type 304 stainless steel with a 4-inch diameter Oldershaw column. Although some preliminary work in glass columns showed considerable promise, the pilot plant unit never functioned smoothly or satisfactorily. Corrosion of the stainless steel was quite serious.

Simultaneously, another installation [126-128], proceeding along similar lines but using only glass equipment, was able to produce a bottoms product containing less than 0.1 percent hafnium/zirconium. The feed was 3 percent hafnium/zirconium. A 1-inch diameter Oldershaw column with 50 plates was used. On redistilling, a product was produced containing approximately 100 ppm of hafnium. One can only hypothesize that the success of this operation resulted in part from the use of glass equipment and from the practice of transferring the feed complex into the column boiler by distillation, which left many of the impurities behind in the feed make-up boiler.

In neither case was a satisfactory procedure developed to recover the zirconium free of phosphorous. One procedure tried was to pass the oxychloride complex vapor through a hot bed of carbon [125] to produce zirconium tetrachloride and phosphorous trichloride, which could be separated by distillation. Although the results were not satisfactory, a recent patent [129] would indicate the successful development of this procedure.

Tetrachlorides

In the most commonly used production procedure, zircon sand is converted into hafnium-zirconium tetrachlorides which are put into aqueous solution as feed for a separation process. The separated metals are recovered as oxides and converted into their respective tetrachlorides for reduction to metal (see Fig. 2.1). Obviously a method of separating the metals by distillation of their tetrachlorides would be a most logical improvement in the production procedure. For this reason, considerable attention has been given to this approach, but the results have not been too promising.

Considerable information is available about the vapor pressures of the zirconium tetrachloride. Scarborough and Plucknett [130] determined the vapor pressure of zirconium tetrachloride by molecular

effusion in the range of 70 to 120° C. The equation for the vapor pressure is

$$\text{Log } P_{mm} = -4438/T + 8.937.$$

Also, the mean molar heat of sublimation was calculated to be 20.3 ± 1.0 Kcal per mole.

Kubn, Ryon, and Palko [131] measured the vapor pressures of zirconium and hafnium tetrachlorides in the range 230–420° C and found the following relationships:

| <i>Vapor pressure</i> | <i>Triple point</i> |
|--|----------------------|
| ZrCl ₄ , $\text{Log } P_{mm} = -5400/T + 11.76$ | 437° C and 14,500 mm |
| HfCl ₄ , $\text{Log } P_{mm} = -5200/T + 11.74$ | 434° C and 25,000 mm |

A very recent patent [132] has been issued for the purification of zirconium tetrachloride by fractional distillation. A mixture of hafnium-zirconium tetrachlorides is fractionally distilled under pressure equal to the equilibrium vapor pressure in the fractionating zone. The boiling liquid temperature in the hot end of the fractionating zone is kept in the range of 455 to 520° C. A zirconium tetrachloride product low in hafnium is removed from the hot end of the fractionating zone, and a product enriched in hafnium tetrachloride is removed from the low temperature end.

Tetrachloride-Fused Salt Solvent

A new variation of the tetrachloride distillation process [133] can be operated at atmospheric pressure. The use of stannous chloride as a solvent for the tetrachlorides provides a liquid phase for conventional distillation procedures. Most important, the stannous chloride does not form addition products with the tetrachlorides at the operating temperatures, so that complete separation is possible. Single stage separation factors of almost 2 can be obtained.

A liquid feed solution containing 1 part of mixed hafnium and zirconium tetrachlorides dissolved in 2 parts of molten stannous chloride at 260° C is introduced into the middle of a distillation column. Molten stannous chloride is also fed in at the top of the column. Temperatures in the column range from 250° C at the top to 450° C at the bottom. Hafnium tetrachloride vapors are taken from the column top. Zirconium tetrachloride-stannous chloride solution from the reboiler is passed through a stripping column at 600° C to recover the zirconium tetrachloride. Considerable corrosion may occur with this system also.

A recent patent [134] proposes a fused-salt system using alkali and alkaline earth chlorides as a liquid phase. Hafnium enrichment only is claimed. Studies by the U.S. Bureau of Mines [135] lead to the conclusion that while some separation or enrichment can be

obtained, the formation of addition compounds such as $\text{NaCl} \cdot \text{ZrCl}_4$ prevents the complete separation of the tetrachlorides by this method.

Other

Hoekstra and Katz [136] prepared borohydrides of hafnium and zirconium by reacting the salts NaHfF_5 or NaZrF_5 with aluminum borohydride. The borohydrides are the most volatile known compounds of hafnium and zirconium. The vapor pressure data shown in Table 2.13 indicate the possibility of separating these materials by distillation.

TABLE 2.13—VAPOR PRESSURES OF HAFNIUM AND ZIRCONIUM BOROHYDRIDES [138¹]

| Temperature (° C) | Hafnium borohydride V.P. (mm) | Zirconium borohydride V.P. (mm) |
|-------------------|-------------------------------------|---------------------------------------|
| | | |
| 0..... | 2.2 | 1.8 |
| 10..... | 4.7 | 4.2 |
| 25..... | 14.9 | 15.0 |
| 30..... | 21.0 | 20.3 |
| 40..... | 36.0 | 33.2 |
| 50..... | 56.4 | 52.2 |
| 118..... | 760.0 | ----- |
| 123..... | ----- | 760.0 |

¹ Courtesy of the *Journal of the American Chemical Society*.

Bradley and Wardlaw [137–139] prepared various alkoxides of hafnium and zirconium and investigated their relative volatilities as a possible means of separating hafnium and zirconium. The boiling points of the alkoxides are shown in Table 2.14.

Although monoxide vaporization is not recommended as the basis for a separation method, the monoxide of zirconium is either more stable or more volatile than the corresponding monoxide of hafnium. As a result, during the electron beam melting of hafnium, a considerable reduction of zirconium content occurs via the mechanism of zirconium monoxide evolution (see Chap. 4).

TABLE 2.14—BOILING POINTS OF HAFNIUM AND ZIRCONIUM ALKOXIDES [139]

| Alkyl (R) | B.P. of $\text{Hf}(\text{OR})_4$ | | B.P. of $\text{Zr}(\text{OR})_4$ | |
|-----------------|----------------------------------|-------|----------------------------------|-------|
| | ° C | P(mm) | ° C | P(mm) |
| Ethyl..... | 180–200 | 0.1 | 180–200 | 0.1 |
| Isopropyl..... | 170 | 0.35 | 172 | 0.35 |
| Tert-butyl..... | 90 | 6.5 | 92.5 | 6.0 |
| Tert-amyl..... | 92 | 0.1 | 95 | 0.1 |

Selective Partial Reduction

Lower halides of zirconium have been known for some time, and some conditions for their formation have been published [140–142]. Possible partial reduction was noted during the Kroll reduction of commercial zirconium tetrachloride (2 percent hafnium) by workers at the U.S. Bureau of Mines. The volatile gases bled from the furnaces tended to be enriched in hafnium, especially near the end of the reduction run.

Although other investigators have succeeded in producing lower halides of hafnium and zirconium by partial reduction, Newnham [143–145] made the first thorough study of these partial reductions with the intent of separating the two metals. Newnham found that under certain conditions zirconium tetrahalide will be reduced to a trihalide while the corresponding hafnium tetrahalide is unaffected. Zirconium or zirconium dihalide are the preferred reducing agents, although zinc, aluminum, or magnesium reportedly can be used.

Crude zirconium tetrachloride is selectively reduced by zirconium or zirconium dichloride at 420°C , producing zirconium trichloride. When the reaction is complete, hafnium tetrachloride and any unreacted zirconium tetrachloride can be sublimed away at $200\text{--}300^{\circ}\text{C}$ in a vacuum. These tetrachlorides may contain up to 30 percent hafnium tetrachloride. Upon heating above 450°C , the zirconium trichloride will disproportionate to mixed dichloride and tetrachloride, the latter being removed by sublimation. The hafnium content of this tetrachloride will be about 0.05 percent. The zirconium dichloride can be reused in the reduction step. The optimum temperature of the reduction is controlled by the reducing agent selected and the operating pressure.

Recent patents [146, 147] by Newnham cover the use of tetraiodides in the above type of separation. The reduction is carried out at 500°C in a previously evacuated vessel; then the unreacted tetraiodides are collected on a cooled surface. The triiodide is disproportionated at 350°C , the tetraiodide being removed by sublimation. Operating pressures are not given.

Since hafnium tetrahalide is not reduced in these processes, no hafnium should be present in the trihalide. Under careful laboratory conditions [144], nonvolatile zirconium trichloride has been produced which contained only 0.01 percent hafnium. This is the greatest separation recorded for one stage of any separation process. Unfortunately, the volatile hafnium tetrahalide product always contains some unreacted zirconium tetrahalide, so that complete separation of the two metals to yield pure hafnium is quite difficult.

This process has the obvious advantage that the hafnium-free zirconium is recovered as the tetrachloride, suitable for reduction to the metal. One difficulty experienced with this process is that the

trichloride tends to form a solid cake over the surface of the reducing agent, requiring either a large surface area or some means of continuously exposing new surfaces. Commercial use of the process has not been announced, but considerable industrial development has been conducted in this country.

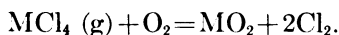
Larson and Luddy [148] investigated the reactions between the metals zirconium and hafnium and their respective halides. All reactions were conducted at 400 to 700° C with a corresponding high pressure. The iodides were most easily reduced, followed by the bromides and chlorides. No reaction was observed with the fluorides. The trivalent halide products disproportionate to the dihalide and tetrahalide, but the reaction rate was slow below 450° C which confirms the data of Newnham regarding the tetrachlorides. Larson and Luddy concluded that under the conditions used, the difference in reduction was not great enough for a metal separation process.

A recent paper [149] on selective reduction using an aluminum reducing agent showed good separation. Two steps of reduction reduced the hafnium content from 2.45 percent to 0.02 percent. However, the zirconium was recovered by aqueous leaching, requiring a chlorination step between each reduction. Here, as in the work of Newnham, a crust formed on the surface of the reducing agent, materially reducing the rate of reduction.

Some work has been conducted on the use of sodium or magnesium to selectively reduce zirconium from the double fluorides leaving an enriched hafnium salt.

Vapor Phase Dechlorination

Using the currently available thermodynamic data, Prakash and Sundaram [150] calculated the free energy change for the following reaction for hafnium and zirconium tetrachlorides:



The data indicated that hafnium tetrachloride should be quite stable while zirconium tetrachloride would be converted to the oxide. The calculated equilibrium pressure ratio $P_{\text{Cl}_2}/P_{\text{O}_2}$ for the oxide formation at 800° C is 3.08×10^3 for the zirconium reaction and 1.06×10^{-5} for the hafnium reaction.

Zirconium tetrachloride containing 2.5 percent hafnia on an oxide basis was sublimed in a chloride atmosphere and led into a heated reaction chamber where it was mixed with a stream of chlorine and oxygen. The nonvolatile oxide dropped to the bottom of the chamber while the unreacted chlorides were carried to condensers. With a chlorine-to-oxygen ratio of 1:2 and a furnace temperature of 800° C, the oxide contained 1.4 percent hafnia after 1 hour and the

volatiles contained about 25 percent hafnia. Similarly, with a chlorine-to-oxygen ratio of 1:1 at a temperature of 500° C, after 2 hours the oxide contained 1.29 percent hafnia and the volatiles contained more than 25 percent hafnia. The zirconia recovery ranged from 90 to 97 percent.

Evans [151] recalculated the free energy changes for the reactions using newer thermodynamic data. The results indicate that the hafnium reaction is appreciable at all temperatures and that a separation is theoretically possible, but with considerably less efficiency than theoretically indicated from the calculations of Prakash and Sundaram. Evans suggested that the mixed chlorides should be reacted with a slight stoichiometric deficiency of oxygen in a closed static system under pressure. The possible formation of oxychlorides was not considered in the above discussions, presumably because zirconium oxychloride is known to decompose at about 350° C. However, some investigators [152] have felt that a stable, volatile hafnium oxychloride may exist.

Electrolysis

French investigators [153] have obtained hafnium enrichment during electrolysis of a fused solution of K_2ZrF_6 and NaCl in a graphite crucible at 850° C in an argon atmosphere. Cathodes were rods of molybdenum, nickel, or iron. The crucible served as the anode. Using a cathode current density of 200 amp/dm², enough current was passed through the cell to theoretically deposit one-tenth of the total metal content of the bath. The zirconium dendrites contained 0.05 percent hafnium whereas the initial K_2ZrF_6 contained 0.6 percent hafnium/hafnium + zirconium. Current density and voltage have no significant influence on the degree of separation. The hafnium content of the dendrites is consistently about 8 percent of the hafnium-zirconium metal ratio in the fused salt over a considerable range of hafnium contents.

Unpublished work in this country in which soluble zirconium-hafnium anodes in fused salt cells were used had similar results [154]. When a metallic anode containing Zr, Ti, and Hf is taken into solution in an electrolyte in a molten alkaline chloride containing lower chlorides of Zr and alkaline metal, the hafnium remains in the anode slime. Metallic zirconium or zirconium chloride substantially free of hafnium is formed at the cathode. Impure ZrO_2 which has been reduced with metal can be used as anode material. The zirconium chloride produced in this operation contained 0.01 percent hafnium from starting anode material containing 1.8 percent hafnium.

Fractional Precipitation

Until the advent of liquid-liquid extraction and ion-exchange techniques, crystallization and fractional precipitation were the most commonly used methods of separating hafnium and zirconium. Of the two, fractional precipitation is generally faster and more efficient for laboratory purposes.

Phosphate Precipitation

Of the fractional precipitation methods, the phosphate precipitation is the most widely used. Both hafnium and zirconium form quite insoluble phosphates in acid solution, with hafnium being less soluble. The complete phosphate precipitation is commonly used to remove hafnium and zirconium from all other metals in acid solution. As a separation method, (1) the metal phosphates are complexed and dissolved in an acid solution, then part of the complex is destroyed, allowing a fraction of the metal to form the phosphate precipitate, or (2) only enough phosphate is added to an acid solution of hafnium and zirconium to precipitate a fraction of the combined metals.

Freshly precipitated zirconium-hafnium phosphates will dissolve in hydrofluoric acid, concentrated oxalic acid, concentrated sulfuric acid, or phosphoric acid. Then the zirconium-hafnium fluo-phosphate complexes can be broken by adding sodium borate, silicate, or other fluoride-complexing agent, allowing the phosphates to precipitate [155]. The hafnium fluo-phosphate complex is less stable than that of zirconium, and hafnium phosphate is less soluble than zirconium phosphate, so hafnium concentrates in the precipitate.

The phosphates dissolved in concentrated sulfuric acid can be reprecipitated upon dilution with water. However, satisfactory filtration of the precipitate requires enough dilution that essentially all of the phosphate is reprecipitated. De Boer's recommended procedure [155] is to divide the original phosphate precipitate into two parts. The first half is dissolved in concentrated sulfuric acid. The second half is dissolved in hydrofluoric acid, then precipitated as hydrous oxides with sodium hydroxide, washed free of fluoride and phosphate ions, and dissolved in concentrated sulfuric acid. The two solutions are mixed, and phosphate precipitation occurs upon dilution with water. Using this method only 12 to 15 fractionations are needed to obtain a practically pure hafnium product.

The oxalate-phosphate complex should be diluted with sulfuric or hydrochloric acid rather than with water. By dissolving the phosphates in cold, saturated oxalic acid, then diluting with hydrochloric acid, a practically pure hafnium product was obtained after 26 fractionations.

Bardet and Toussaint [156] added phosphoric acid ($\frac{1}{2}$ of the amount needed for complete precipitation of the zirconium and hafnium) to a concentrated sulfuric acid solution of the metals, then diluted the solution with water. The precipitates were fused with alkali carbonates or boiled with sodium carbonate. The resulting hydrous oxides were redissolved in concentrated sulfuric acid for further fractionating. After seven fractionations, the hafnium content had been raised from 3 to 90 percent.

Larsen, Fernelius, and Quill [157] prepared zirconyl sulfate by digesting one part of cyrtolite in two parts of concentrated sulfuric acid at 210°C . The dilute water-extracted zirconium sulfate solution and a dilute phosphoric acid solution were simultaneously sprayed into a 10 percent sulfuric acid solution at 70°C . A dense, easily filterable precipitate formed. For the best separation, phosphoric acid equivalent to only 35 to 45 percent of the combined zirconium-hafnium oxide was used. The precipitate reacted with sodium hydroxide-sodium peroxide to yield disodium hydrogen phosphate and zirconium-hafnium peroxides. The peroxides were readily soluble in sulfuric acid. In this manner the hafnium content of an oxide mixture was increased from 13 to 93 percent in seven fractional precipitations. The product yield was 10 percent of the original hafnium content. Similarly, a hafnium-free zirconium sulfate solution was produced by two precipitation stages, starting with 2–3 percent hafnium to zirconium material and precipitating 60 percent of the combined oxides in each stage.

Willard and Freund [158] hydrolyzed triethyl phosphate in 6N sulfuric acid containing zirconium-hafnium sulfates. The precipitated compound was hafnium ethyl acid phosphate— $\text{HfO} [\text{H}(\text{C}_2\text{H}_5)(\text{PO}_4)] \cdot 2\text{H}_2\text{O}$. The slow hydrolysis ensures a low phosphate ion concentration resulting in a more selective precipitation of hafnium and, necessarily, a very slow rate of production. The superiority of the precipitation from homogeneous solution can be seen from the separation factors [159] which averaged 4.5 for the phosphoric acid compared with 6.3 for the triethyl phosphate. Trimethyl phosphate was suggested as a more easily hydrolyzed phosphate. The optimum fraction of combined oxides to precipitate for maximum separation and recovery varies with the hafnium content of the starting oxide. In one series of five precipitations, 215 g of oxide containing 16.0 w/o hafnia were enriched to 7.16 g of oxide containing 91.1 w/o hafnium, which was a 23.8 percent recovery of the original hafnium content.

The homogeneous solution precipitation was employed by later researchers [160] using both triethyl phosphate and acid ethyl phosphate. Also, a pilot plant development using triethyl phosphate was in operation for a short time [161].

Willard and Freund [158] also demonstrated that the separation is dependent on the ionic form of the zirconium-hafnium in solution as well as the relative solubility of the phosphates. On precipitating one-third of the total oxides from a 6 N acid solution, the following portions of the hafnia were removed from solution:

| | |
|-------------------------|-------|
| Sulfuric Acid ----- | 0.623 |
| Nitric Acid ----- | 0.516 |
| Hydrochloric Acid ----- | 0.513 |

This is in agreement with the data given by Blumenthal [162] indicating the zirconium is in an anion complex in sulfuric acid solutions but is present as a cation in hydrochloric acid.

The arsenates and antimonates react analogously to the phosphates [163] but are not so insoluble as the phosphates. The separations show no advantage over the phosphate precipitation, and the precipitates are difficult to filter. Gump and Sherwood [164] obtained a more crystalline arsenate precipitate by using the homogeneous solution precipitation technique. The arsenate was formed in solution by slowly oxidizing sodium arsenite with nitric acid. No information is available to indicate whether this procedure would increase the effectiveness of the separation obtained by partial precipitation of the arsenates.

Ferrocyanide Precipitation

In 1932 Prandtl [165] proposed the following procedure which does not require the strong acid solutions of the phosphate precipitations. Ammonium sulfate is added to a boiling solution of zirconium-hafnium sulfates, then 200 cc of cold saturated oxalic acid solution is added for every 100 g of oxide in solution. To the warm solution, sodium ferrocyanide is slowly added while stirring. After several hours a yellow precipitate forms. The precipitate, enriched in hafnium, can be converted into hydrous oxides using sodium hydroxide and redissolved in sulfuric acid to continue the process. In three steps, Prandtl claims to have gone from 400 g containing 25 percent hafnium oxide to 27 g containing about 90 percent hafnium oxide.

Schumb and Pittman [166] made a detailed study of Prandtl's ferrocyanide separation method. They determined the effect of dilution and acid concentration and various proportions of ammonium sulfate, oxalic acid, and sodium ferrocyanide on the hafnium separation. The following procedure was recommended for maximum separation:

To a solution of 100 g of oxychloride in 300 cc of water is added 30 cc of concentrated sulfuric acid, 100 g of ammonium sulfate, and 100 cc of oxalic acid saturated solution at room temperature. The resulting solution should be clear, but, if a white precipitate forms,

an additional 50 cc of water should make the solution clear if left standing. A solution of 50 g of sodium ferrocyanide in 50 cc of water is then added dropwise from a buret over a period of several hours while the zirconium-hafnium solution is being stirred vigorously. The yellow precipitate formed during the foregoing step should be left standing for at least an hour before filtration. The zirconium-hafnium ferrocyanides can be reacted with ammonium hydroxide to form zirconium-hafnium hydroxides.

Caustic Leaching

The more amphoteric nature of hafnium has been utilized in caustic leaching of precipitated hydrous oxides [171]. The following tabulation, determined by radioactive tracer techniques, gives the relative solubilities of the hydrous oxides:

| Hydrous Oxide | Solubility (g/l) | |
|--|----------------------------|---------------------|
| | 2 N NH_4OH | 1.8 N NaOH |
| $\text{ZrO}_2 \cdot 2\text{H}_2\text{O}$ | 0.002 | 0.03 |
| $\text{HfO}_2 \cdot 2\text{H}_2\text{O}$ | 0.0003 | 0.24 |

Using the foregoing procedure, in four successive ferrocyanide precipitations the hafnia content of an oxide mixture was enriched from 12 to 80 percent. The recoveries are low because only 15 percent by weight of the oxides are precipitated in one precipitation.

Peroxide Precipitation

The hydrous oxides and phosphates of zirconium and hafnium dissolve easily in hydrogen peroxide and sodium hydroxide forming sodium perzirconate and perhafnate. Upon heating these solutions, zirconium and hafnium precipitate as hydrous oxides. De Hevesy [167] and Rose [168] state that the perzirconate is less stable than the perhafnate, while de Boer [163] found that the perhafnate decomposes more easily. The formation of zirconium peroxysulfate, but not hafnium peroxysulfate, is claimed [169] upon the addition of an excess of hydrogen peroxide to a sulfate solution of the metals. Recently, however, Duke and Bremer [170] have shown that the peroxides of zirconium and hafnium have the same solubility and stability toward decomposition to the hydrous oxide. Similarly, both peroxysulfates exist and have similar properties.

After a zirconium-hafnium solution containing 1.8 percent hafnia was precipitated with strong sodium hydroxide and the precipitate filtered off, the filtrate contained 40 percent of the original hafnium, and the hafnia content was 36 percent of the total oxides in the filtrate. Further development [172] showed that higher temperatures increased the hafnium recovery. The presence of anions such

as carbonate, fluoride, or sulfide materially increased the recovery, but with a slight decrease in the degree of enrichment. The presence of sodium silicate represses the hafnium solubility.

Thermal Decomposition

Differences in thermal stabilities of the compounds of zirconium and hafnium were mentioned by de Hevesy [173] who stated, "While zirconium sulfate begins to decompose above 400° C, the temperature at which hafnium sulfate undergoes marked decomposition lies about 100° higher." Subsequent leaching should enable some separation but has never been developed as a practical process.

Fusion

Fusion of pure zirconium or hafnium pyrophosphates with reagents such as sodium sulfide; sodium sulfide and ammonium chloride; ammonium chloride and magnesium carbonate; barium chloride and magnesium carbonate; magnesium chloride; or calcium carbonate and sodium hydroxide has been used in a study [174] of separation procedures. The fusion products were leached with dilute hydrofluoric acid. With the sodium sulfide or magnesium carbonate and ammonium chloride mixture fusions, the hydrofluoric acid filtrate contained about 90 percent of the zirconium, but only about 50 percent of the hafnium was leached out under similar conditions. This was therefore suggested as a method for separation.

Ion Migration

Kendall and West [175] tried to separate zirconium and hafnium by an ionic migration method. The elements were not amenable to separation in the form of positive ions because of hydrolysis. Fluoride, sulfate, and oxalate complex anions were tried, with the oxalate being most suitable. After several days migration, analysis showed a very slight accumulation of hafnium toward the anode, but the mobilities of the complex anions were evidently so similar that a complete separation was impractical.

Paper Chromatography

A mixed nitrate solution [176] was eluted down strips of Whatman's No. 1 or No. 3 paper using a dichlorotriethylene glycol-nitric acid mixture for a solvent. After 18 hours, the separated band locations were determined by spraying with an alizarin-ethyl alcohol solution. Zirconium progressed more rapidly than hafnium. Detection of 2 μg of each metal was possible, as well as estimation of the relative proportion of each metal. Earlier work [177] was done

with ethyl ether-nitric acid mixtures and also with 2-ethyl n-butyl cellosolve and ethyl acetate.

Diffusion

Separation of zirconium and hafnium by differences in the diffusion rates of their volatile compounds would seem to offer possibilities. A research contract was granted to the University of Tennessee in 1957 to try such a separation using a horizontal thermal diffusion column [178]. However, McTaggart and Newnham [179] mention that diffusion experiments were not successful.

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Chapter 3

HAFNIUM REDUCTION PROCESSES

By E. W. SMITH ¹ AND W. W. STEPHENS ¹

3.1 HISTORICAL

General

Because hafnium was not discovered until 1922 [1], the reduction of hafnium compounds to metal naturally occurred very much later than the reduction of titanium and zirconium. Even after the discovery of hafnium, the very difficult problem of separating hafnium and zirconium resulted in availability of only very small quantities of hafnium compounds with which to work, and these quite often contained considerable zirconium.

Professor C. James of the University of New Hampshire reduced a "hafnium salt" to metal in 1924, but through an interchange of fractions by careless workmen the salt actually contained a considerable amount of zirconium [2].

A survey of the literature indicates that while a great many reduction processes were tried on zirconium compounds, relatively few were tried on hafnium compounds. Again it might be said that zirconium is, comparatively, a much "older" element, and a great deal of interest was not directed toward its production until after World War II. Another reason for less experimental work having been done with hafnium is its close chemical similarity to zirconium, resulting in the assumption that reactions which succeeded or failed with zirconium would behave in a similar manner with hafnium. Underlying all this is the fundamental fact that a scarcity of hafnium compounds precluded major work.

From the onset of reduction of hafnium compounds to metal, the product has been quite brittle. Reduction procedures used to produce good quality, highly ductile zirconium fail to yield comparably ductile hafnium. Embrittlement is the result of the presence of interstitial contaminants, especially oxygen. For a given weight percentage of oxygen, hafnium is less ductile than zirconium [3].

¹ Carborundum Metals Co.

Although some investigations were made in the period from 1923 to 1951, it was not until January of 1951 that the first serious effort was made to produce large quantities of hafnium metal [4]. In fact, it was not until that time that a reasonably good separation of hafnium from zirconium was effected. Even then the first few pounds of "hafnium" produced at the U.S. Bureau of Mines Station at Albany, Oregon was 28 percent hafnium and the remainder zirconium. With a few months another shipment, this time 350 pounds, of 99 percent hafnium oxide was reduced to hafnium metal by the Kroll method in which the tetrachloride was reduced with magnesium. During the first year of production at the Bureau, 8,634 pounds of hafnium oxide were utilized to produce 3,075 pounds of clean sponge. Actual production techniques were almost identical with those used in zirconium production.

Reduction to Lower Halides

Some research has been done on the reduction of the hafnium tetrahalides to trihalides [5]. The purpose of the investigation was to determine the relative ease of reduction of the four halides as: $\text{Hf} + 3\text{HfX}_4(\text{g}) \rightarrow 4\text{HfX}_3(\text{s})$. Formation of the lower halides was favored by increasing temperature in the range of 200–700° C and/or by increasing pressure in the range of 5–15 atm. HfF_4 could not be reduced to hafnium, but ease of reduction increased from the chloride to the iodide.

Reduction of Fluorides

The first hafnium metal ever produced, which is credited to de Hevesy, was made by the reduction of potassium hafnium hexafluoride with sodium as the reductant [6, 7]. Reduction of hafnium tetrafluoride with calcium has been made in 6-inch diameter and 21½-inch diameter steel containers lined with calcium fluoride [8].² The charge for the smaller reactor consisted of 350 g of HfF_4 , 275 g I_2 , 192 g Ca, and 65 g Zn. Biscuits of hafnium-zinc as large as 16 pounds were made in the larger reactor. Zinc was used to obtain a low enough melting point alloy to allow the hafnium to be consolidated into a single mass rather than dispersed throughout the charge as sponge or beads. Zinc was removed from the hafnium-zinc alloy biscuit by heating slowly to 1,800° C in a graphite crucible under vacuum. The over-all yield after reduction and dezincing was 97 percent. Some of the sponge hafnium was arc-melted producing an ingot with a hardness of 69 Rockwell A.

² Process description from Ref. 8 courtesy of the Electrochemical Society.

The ingot was hot rolled but was too brittle to be easily cold worked. Analytical results from this ingot are listed in Table 3.1. Although oxygen content of the sponge was not determined, the statement was made that it was undoubtedly present in considerable amounts as indicated by the extreme brittleness of the material.

TABLE 3.1—INGOT ANALYSIS

| <i>Element</i> | <i>w/o</i> |
|----------------------|----------------|
| Ca..... | <0. 01 |
| Fe..... | <0. 01 |
| Mg..... | <0. 01 |
| Si..... | <0. 01 |
| Zn..... | <0. 002 |
| Zr..... | <0. 01 |
| C..... | 0. 07 |
| N ₂ | 0. 05 |
| O ₂ | Not determined |

Another series of bomb reductions was made on hafnium tetrafluoride at Oak Ridge National Laboratories using calcium as the reductant with iodine as a booster [7]. The reaction mixture was contained in a tamped calcium fluoride liner within a steel container. A cover of calcium fluoride was placed over the mix and then enclosed by a bolted steel cover. A rod of molybdenum, tungsten, or tantalum was pushed laterally through sleeves provided in the chamber so as to be in contact with the charge. Evacuation followed by backfilling with the argon was repeated several times, and then the unit was sealed under one atmosphere pressure of argon. The reaction $\text{HfF}_4 + 3\text{Ca} + \text{I}_2 \rightarrow \text{Hf} + 2\text{CaF}_2 + \text{CaI}_2$ was initiated by passing a current through the rod. This highly exothermic reaction generated sufficient heat to fuse some of the reduced hafnium in the bottom of the reaction vessel. A dense button was not obtained in these reactions even though some yields were good. The high melting point of the hafnium metal was considered to be the principal cause of porous buttons. Analytical results from this button are listed in Table 3.2.

TABLE 3.2—ANALYSIS OF HAFNIUM METAL (Hf-2 w/o Zr) [9]

(Impurities in ppm)

| | | | | | |
|---------|-------|---------|------|---------|------|
| Al..... | 400 | Cu..... | 20 | P..... | <100 |
| B..... | 10 | Fe..... | 200 | Pb..... | 10 |
| Ba..... | <100 | Li..... | <100 | Si..... | 100 |
| Be..... | <0.02 | Mg..... | 100 | Sn..... | <10 |
| Ca..... | 300 | Mn..... | 10 | Ti..... | 4 |
| Cd..... | <2 | Mo..... | 10 | V..... | 10 |
| Co..... | <10 | Na..... | <100 | Zn..... | <100 |
| Cr..... | 10 | Ni..... | 10 | | |

Reduction of Oxide

Early work involved the reduction of hafnium oxide to metal with several different reductions. De Boer and Fast [10] indicated that reduction of hafnium oxide to metal was superior to the reduction of hafnium tetrachloride to metal because of the difficulties encountered in the intermediate chlorination of the oxide. They reduced the oxide with both Ca-Na and Mg-Na. The results of the reductions showed that the separation of hafnium and zirconium was not complete, and fractionation was believed to have occurred during chlorination. In one case, the hafnium oxide was reduced with calcium and sodium to the crude metal and subsequently purified by the iodide process to produce bars of hafnium having a density of 12.62 g/cc which is equivalent to 90 a/o hafnium. In the second case, the hafnium oxide was chlorinated, and the resultant tetrachloride was reduced to crude metal using the same reducing agents (Ca and Na) as in the first instance. Subsequent iodide purification of the metal resulted in bars with a density of 11.75 g/cc.

The comparison of hafnium metal reduced from the oxide and the tetrachloride indicated that the iodide bars reduced from the starting material of hafnium tetrachloride consistently had a more lustrous and cleaner appearing surface than the iodide bars produced from metal reduced directly from the oxide. In the investigations of de Boer and Fast, the surface appearance of hafnium bars never was as good as that obtained on zirconium bars.

From one series of phosphate fractionations in the separation of hafnium from zirconium, the highest fraction was considered to contain 100 percent hafnium in the oxide produced. Seventy grams of the oxide, when reduced with a mixture of calcium and sodium, yielded 53 g of hafnium metal. The metal was divided into ten portions and purified by the iodide process to 35.5 g of hafnium rod with densities ranging from 13.02 to 13.1 g/cc; however, the ductility of all the rods was very low.

The reduction of hafnium oxide was said to have taken place completely and quickly when hafnium carbide was introduced into the melt of pure metal followed by the addition of hafnium oxide in the solution [1]. Heraeus Vacuumschmelze A-G (1933) used a vacuum-induction furnace for this type of reduction.

Even though many reductions of small samples of hafnium oxide were made by investigators and some hafnium metal appeared as good as that reduced from the halides, particularly the tetrachloride, later investigations completely bypass hafnium oxide as a starting material. Regardless of how complete the reduction of hafnium oxide seems to be, the hafnium metal is embrittled. As with other reactive metals in which a very small amount of oxygen contamina-

tion has a detrimental effect on the properties of the metal, it seems that the direct reduction of hafnium oxide to the metal will never be commercially feasible.

Reduction of Tetrachloride

The reduction of hafnium tetrachloride to crude hafnium metal has been utilized since shortly after the discovery of hafnium. De Boer and Fast made several reductions of hafnium tetrachloride, but, as previously mentioned, the chlorination of hafnium oxide was difficult, and, as a result, they preferred direct reduction of hafnium oxide to that of hafnium tetrachloride [10].

However, despite the fractionation and difficulties in chlorination of hafnium oxide, the subsequent iodide bars produced via the tetrachloride had slightly more ductile properties. The purest hafnium, that is, metal with the highest density (13.31), was prepared by rechlorinating crude hafnium metal with a density of 12.9–13.1 and then subliming the tetrachloride three times in hydrogen atmosphere to produce dense white hafnium tetrachloride crystals. The tetrachloride was reduced with sodium, then the crude metal was purified by the iodide process. One iodide bar was somewhat ductile and had a density of 13.14 with 97.5 a/o hafnium [10].

The reduction of the tetrachloride was carried out in an iron cylinder into which a second cylinder was inserted and pressed firmly against the mixture of HfCl_4 and Na. The cylinders were then welded together. The purpose of compressing the mix was to eliminate the maximum amount of air. The cylinders were then heated in an electric furnace to 850°C with a considerable exothermic effect during the reaction. Upon removal of the products the metal was found to have sintered. The crude hafnium was washed with alcohol, then water, and finally in boiling hydrochloric acid [1].

Litton [7]³ describes the preparation of crude hafnium metal by reacting a 10 percent stoichiometric weight excess of magnesium powder with hafnium tetrachloride in a stainless steel reactor in which an annealed silver gasket was used for compression sealing. External heating to 650°C was used to initiate the reaction. The reaction products were removed and leached with 5 percent hydrochloric acid followed by a distilled water wash and sizing through a 20 mesh screen. The +20 mesh hafnium was purified by the iodide process, and the -20 mesh was oxidized and returned to the chlorinator.

The range of spectrochemical analysis of 7.5 pounds of four lots of low-zirconium hafnium sponge which represents a 72 percent recovery from the oxide is listed in Table 3.3.

³ Process description from Ref. 7 courtesy of the Electrochemical Society.

from the distillation retort and in subsequent handling to prevent losses.

Large-scale production of hafnium sponge has been carried out at only three locations in the United States: first, at the U.S. Bureau of Mines Station in Albany, Oregon, where the earliest reductions were made in 1951, and later at the Akron, New York, plant of the Carborundum Metals Company, and the Albany, Oregon, plant of the Wah Chang Corporation. Production ceased at the Bureau of Mines in January 1955.⁴

At the Bureau of Mines, until recently, separate steps and equipment were used for purification of the chloride and subsequent reduction to metal, while at the Carborundum Metals Company the combination purification-reduction technique is used.

Bureau of Mines Operation

Hafnium production operations at the U.S. Bureau of Mines, Albany, Oregon, have been described by Holmes, Barr, and Gilbert as follows:⁵

The raw chloride is charged (with baffles to promote heat transfer) into an Inconel can 25 inches in diameter and 40 inches high (Fig. 3.1). This can and chloride are then lowered into the pit-type furnace containing three heating zones—the lower or subliming zone, the middle or condensing zone, and the lead-seal zone. A floating top is immediately set in the furnace, and the lead-antimony seal is frozen. Paraffin added and frozen on top of the lead completes the seal, and the furnace is evacuated to 25 mm of Hg with the lower zone set at 250° C. The furnace is backfilled with helium, and after 1 hour of soaking at this temperature the evacuation is repeated. This conditioning is to remove combined water and the more volatile chlorides, such as the chlorides of titanium and silicon.

The lead seal is melted, and the lower zone temperature is gradually raised while the expanding gases and volatile impurities are bled off. Air and then water cooling are applied to the coils to collect the purified dense chloride.

The temperature at which sublimation is carried out has been lowered and the purification time lengthened from that used in the

⁴ Currently the Atomic Energy Commission has the hafnium oxide produced by its zirconium producers, the Carborundum Metals Company, Columbia-National Corporation, the Mallory Sharon Metals Corporation, and Wah Chang Corporation, converted by the Wah Chang Corporation to the tetrachloride by the fused salt process and reduced with magnesium to sponge metal. The Wah Chang Corporation, the Mallory Sharon Metals Corporation, and the Carborundum Metals Company employ the hexone-thiocyanate process for the hafnium-zirconium separation, while the Columbia-National Corporation uses the tributyl phosphate process.

⁵ The italicized text is quoted from Ref. 13.

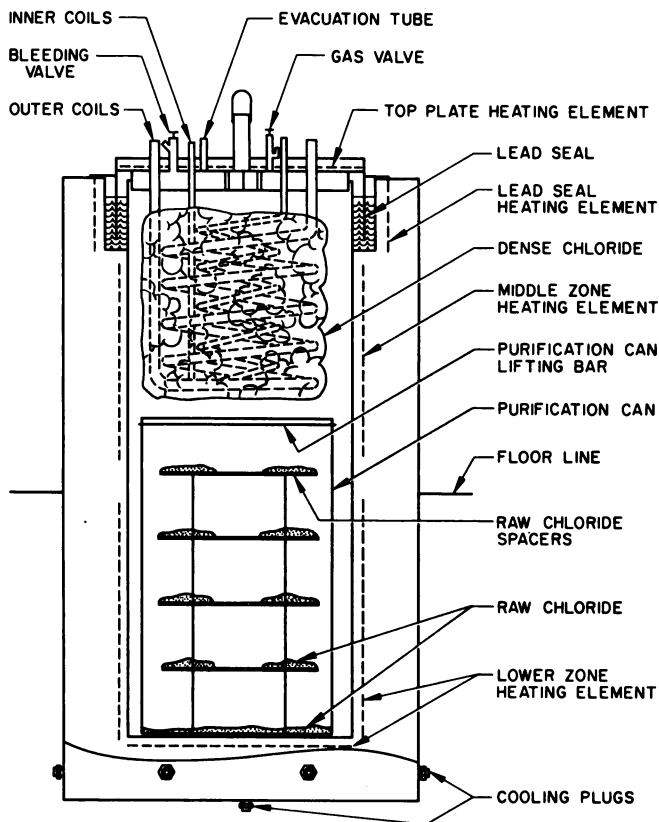


FIGURE 3.1. Assembly of Purification Furnace (from USAEC—*The Metallurgy of Zirconium*, B. Lustman and F. Kerze, Jr., eds., McGraw-Hill, New York, 1955).

purification of zirconium owing to the possibility, at a high temperature, of carrying over oxychloride to the dense chloride. A temperature setting on the lower zone (subliming zone) of 575° C has been found adequate for maintaining the optimum rate.

The reduction of hafnium tetrachloride with magnesium is made in zirconium plant equipment without modification.

After the purification has cooled sufficiently, the top with dense chloride on the coils is removed (Fig. 3.2) and placed in the reduction furnace which contains a mild steel crucible 25 inches in diameter and 20 inches in height. This crucible contains 140 percent of the theoretical magnesium required for reaction with the dense chloride and is covered with a baffle (as shown in Fig. 3.3) to exclude any oxide residue falling from the coils. The furnace is sealed as in the purification and evacuated to 3 mm. of Hg with water cooling maintained on the coils, then backfilled with helium. This is repeated, then the lead seal is melted, the lower zone set

to 775°C , and the floating top to 450°C . Again the furnace is bled as the gases expand and the chloride begins to sublime. When the magnesium has melted, the HfCl_4 is sublimed by heating the middle zone and reacts with the molten magnesium in the crucible. The sublimation rate is controlled by the middle zone heating element and air on the coils. During the initial reaction, which lasts 4 to 5 hours, the zone temperatures are controlled by additions



FIGURE 3.2. Dense Purified Hafnium Tetrachloride Condensed on Coil Attached to Purification-Reduction Furnace Top; Relative Location of Crucible and Baffles for Reduction Operation Is Shown.

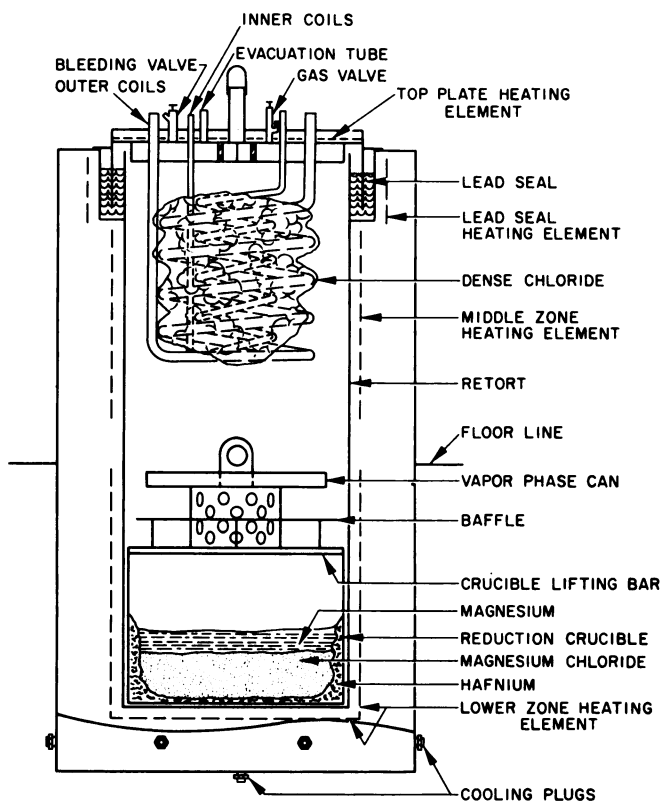


FIGURE 3.3. Assembly of Reduction Furnace (from USAEC—*The Metallurgy of Zirconium*, B. Lustman and F. Kerze, Jr., eds., McGraw-Hill, New York, 1955).

of helium, so that the furnace runs 50°C cooler than in a corresponding zirconium reduction, which is permitted to rise to 875°C . This has been found to give a cleaner reduction and higher recovery of usable sponge. After the reduction is over, which is indicated by the necessity of adding helium to keep the floating top floating, the zone temperature at the reduction crucible is now raised to 920°C and held for 1 hour. Any hafnium sponge that may be on the sidewalls of the crucible, above the magnesium chloride cover, appears to be cleaner if this high finishing temperature is employed, and reduction byproducts are less pyrophoric when exposed to the atmosphere at the time of transfer to the salt-removal furnace.

In the reduction furnace the hafnium sponge is obtained as a magnesium saturated paste. In the distillation furnace (Fig. 3.4) where the crucible is inverted, the sponge usually slumps and rests on the table. Some difficulty is experienced in removing the distilled sponge from the furnace, since when the crucible is removed,

the sponge remains on the table rather than staying in the pot where it can be protected from burning by an inert atmosphere. Due to the pyrophoric nature of the material, a self-locking table was devised to take the place of the standard table. This is placed in the crucible and locked by two crossed rods when the crucible is transferred from the reduction to the distillation furnace. This self-locking table prevents movement of the sponge mass, keeping it confined within the crucible, and consequently prevents fires as the crucible is being handled after distillation.

Before the retort is opened the sponge is conditioned with air. This conditioning process begins at about 37° C and is necessary to passivate the sponge surface so that it will not ignite upon exposure to the normal atmosphere. To condition a charge, dry air is admitted slowly into the retort while the temperature is watched carefully. When atmospheric pressure is reduced, the air is immediately pumped out again. Room air is then admitted slowly and allowed to remain for 1 hour before being pumped out.

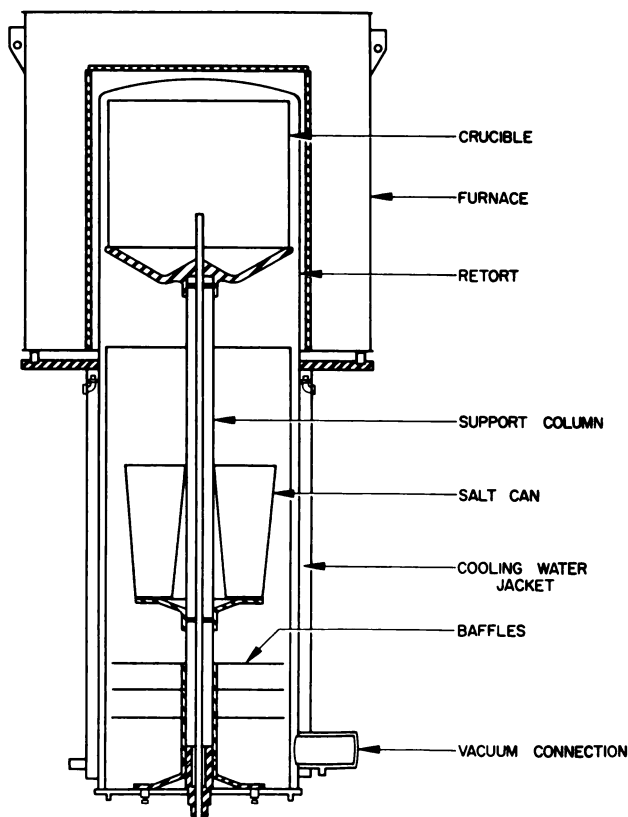


FIGURE 3.4. Distillation Furnace (from USAEC—*The Metallurgy of Zirconium*, B. Lustman and F. Kerze, Jr., eds., McGraw-Hill, New York, 1955).

The retort is then filled with helium and is ready to open. This conditioning period requires approximately 4 hours, which is 1 hour longer than is required for zirconium.

A helium-atmosphere box for cleaning the sponge was equipped with a power driven buffer. All sponge that had been in contact with the crucible or table was cleaned by wire brushing, and the sponge crushed and sized without the benefit of an inert atmosphere. The exercise of extreme care in all operations consistently produces a sponge similar in appearance and ease of handling to zirconium sponge. Very carefully controlled runs give a higher efficiency, and the sponge shows crystal growth more nearly equal to that of zirconium.

Table 3.4 gives recoveries for a typical run in the Bureau of Mines reduction plant [13].

TABLE 3.4—RECOVERIES FOR TYPICAL RUN [13]

| PURIFICATION STEP | | Pounds | Recovery (%) | |
|-------------------|--------------------------------------|--------|--------------|--|
| Input: | Raw HfCl_4 | 543 | ----- | |
| Output: | Weight of dense chloride | 509 | 93. 7 | |
| | HfO_2 (oxide residue) | 27 | 5. 0 | (recycled) |
| | Loss, handling | 7 | 1. 3 | |
| | Total | ----- | 100. 0 | |
| REDUCTION STEP | | | | |
| Input: | HfCl_4 (dense) | 509 | ----- | |
| | Magnesium (40% excess) | 127 | ----- | |
| Output: | Absorbed HfCl_4 | 496 | 97. 4 | |
| | Vapor phase | 4 | 0. 8 | |
| | Loss, handling | 9 | 1. 8 | |
| | Total | ----- | 100. 0 | |
| DISTILLATION STEP | | | | |
| Input: | Net weight, crucible contents | 623 | ----- | |
| Output: | Hafnium sponge | 268 | 96. 5 | (of theoretical in dense sponge) |
| | MgCl_2 and excess Mg | 355 | ----- | |
| | Over-all recovery | ----- | 88. 3 | |

Carborundum Metals Company Operation

In the production of hafnium sponge at the Carborundum Metals Company, the same furnaces [14] are used for purification and reduction as in zirconium production. The retorts of these furnaces are made of $\frac{1}{4}$ -inch thick, Type 310 stainless steel and are 40 inches ID by 3 feet 8 inches high. The furnaces are mounted in the second floor in such a manner that they extend some four feet above the floor and the remainder below the floor. The three independently

controlled heating zones for each electric furnace are arranged to supply heat to the crucible, the tetrachloride charge can, and the coil area (Fig. 3.5).

Loading of the furnace is accomplished by placing the Type 430 stainless steel crucible, which contains the stoichiometric plus 60 per cent excess acid-pickled magnesium ingot, onto the lowered hydraulic loading ram; placing a baffle on top of the crucible; and then placing the Inconel charge can with 2,000 pounds of hafnium tetrachloride on the baffle. The entire assembly is then raised up onto the retort and the retort bottom is bolted to the retort. An O-ring gasket in the retort bottom acts as a vacuum tight seal. The tetrachloride cans are handled as quickly as possible when uncovered to reduce the air-tetrachloride contact time.

Evacuation of the retort to 30 mm Hg pressure by means of a water eductor is followed by a helium backfill. After repetition of this cycle, the temperatures are raised, and the chloride conditioning

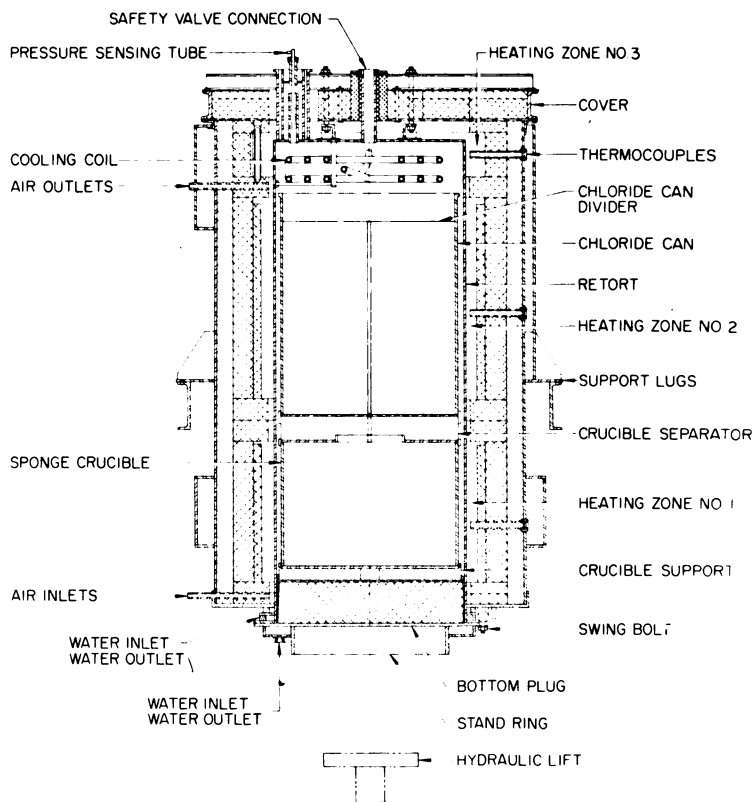


FIGURE 3.5. Purification-Reduction Furnace (Courtesy of Carborundum Metals Co.).

procedure is carried out. The lower zone temperature is then raised to melt the magnesium after which the middle zone temperature is raised to sublime the hafnium tetrachloride from the charge can down into the molten magnesium in the crucible. By automatically controlling the air flow through the cooling coils which are located directly above the tetrachloride charge can, the pressure within the retort can be maintained at about one psig. The maximum lower zone temperature is 850° C since a eutectic forms between the iron in the crucible and the hafnium regulus if higher temperatures are used.

Completion of the reduction is indicated by a pressure drop which is indicative that the supply of tetrachloride is exhausted. Helium is added when low pressure develops at the end of the reaction to prevent the lead seal from being pushed into the retort. Water is passed through the coils upon completion of the reaction to condense any tetrachloride which may not have reacted. Material on the coils makes up part of the charge for the subsequent reduction. Air is passed through the space between the retort wall and the electric heating coils to aid in the cooling. From 6 to 10 hours are required for cooling. Upon removal of the retort bottom, the entire assembly is lowered, and the crucible is covered and quickly moved to the distillation retort or to a holding pot which is then evacuated and filled with inert gas.

The distillation is carried out in the following manner [14, 15]. Following the removal of the crucible from the reduction furnace (or from the holding pot in the case when a distillation furnace is not immediately available) it is loaded into a bottom-charged vertical distillation furnace by means of a hydraulic ram. The inverted crucible rests on a baffle which in turn rests on a salt-catcher can. A special precaution of fastening the baffle to the crucible is practiced to prevent movement between these units when the furnace is unloaded. This is done because there is usually sponge resting on the baffle after distillation which can be easily ignited by friction during unloading of the retort. Portable, bell-type electric furnaces are used to supply the heat to the ¾-inch thick Type 310 stainless steel and Inconel retort. The lower section of the retort is mild steel and is surrounded by a water jacket to provide a condensing surface for the magnesium and magnesium chloride removed by distillation.

Vacuum pumping systems are provided for both the inside and outside of the retort to prevent retort distortion during the low pressure distillation. The inside vacuum is maintained with an oil-jet booster-diffusion pump backed by a 130-cfm mechanical pump.

The space between the retort and the bell heating furnace is evacuated by a 27-cfm mechanical pump to about 1 mm of Hg.

When the loading of the retort has been completed and the bottom plate bolted to the lower retort flange, the retort is evacuated, leak checked, and then heated to 850°C . First, the MgCl_2 and magnesium melt and run into the salt can, at which point the temperature is raised to 960°C and held for 24 hours to assure removal of residue from the sponge by distillation. After the power has been turned off, the retort is backfilled with helium while the pressure outside the hot retort is equalized with plant air. The bell furnace is then removed and the retort allowed to cool to room temperature.

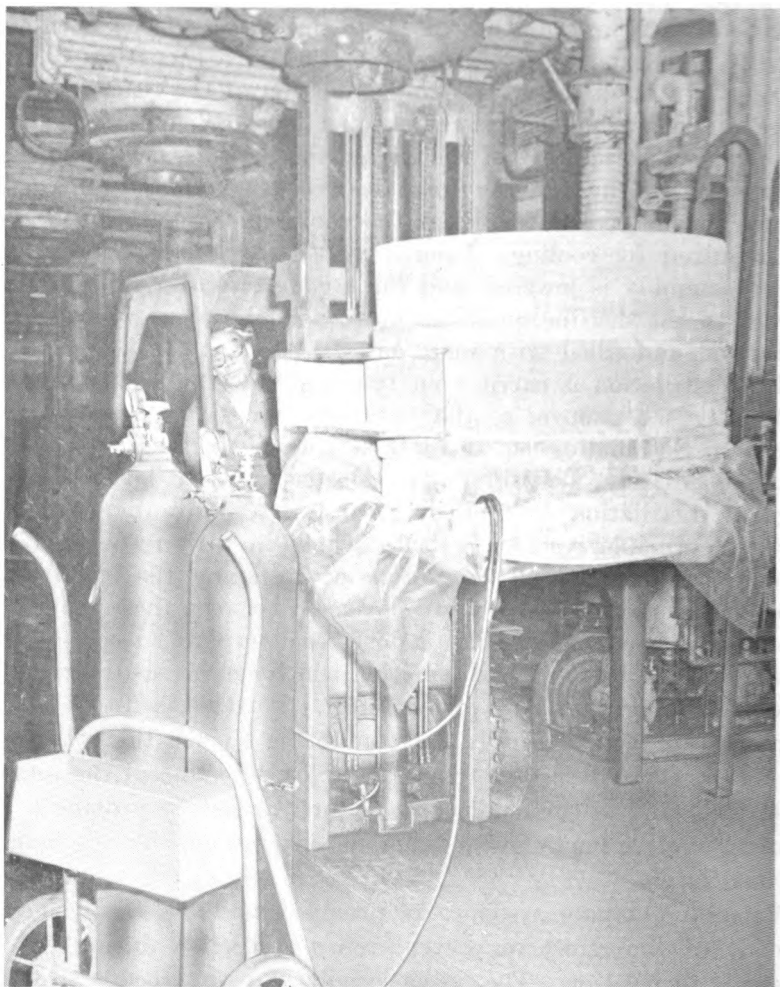


FIGURE 3.6. Crucible of Hafnium Sponge Being Removed from a Distillation Furnace at Carborundum Metals Co., Akron, N.Y. Note: An Inert Atmosphere Is Maintained to Prevent Ignition (Courtesy of Carborundum Metals Co.).



FIGURE 3.7. Distilled Hafnium Sponge Being Removed from a Crucible at Carborundum Metals Co., Akron, N.Y. (Courtesy of Carborundum Metals Co.).

Prior to opening the retort, plant air is slowly bled in to allow the surface of the sponge to oxidize active centers at a controlled rate. This treatment is usually termed "conditioning." A close check is kept on the retort temperature so that oxidation does not occur too rapidly and ignite the entire crucible of sponge. An immediate helium backfill will stop rapid oxidation if a temperature rise is noted. After the sponge is conditioned, the furnace is opened, and the inverted crucible, baffle, and sponge are covered with a polyethylene bag into which a hose for inert gas has been inserted (Fig. 3.6). The bag over the sponge is purged with inert gas continuously as the crucible is moved from the retort to a holding pot where the sponge is kept under a vacuum for about 24 hours until it has cooled to room temperature.

After the crucible is removed from the holding pot, some 1,000 pounds of sponge are broken out of the crucible (Fig. 3.7). The sponge chunks are placed on a stainless steel pan and crushed with a hydraulic chisel while a purge of inert gas is maintained on the crushing area (Fig. 3.8). The sponge chunks are cut into 2-inch

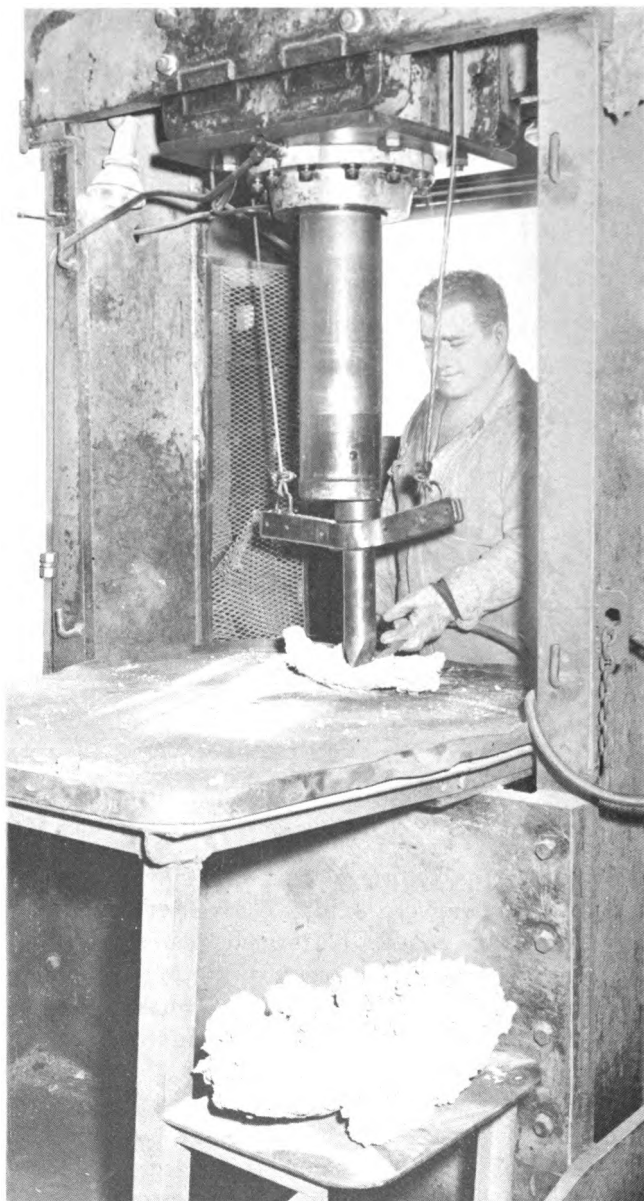


FIGURE 3.8. Breaking Hafnium Sponge at Carborundum Metals Co., Akron, N.Y.
(Courtesy of Carborundum Metals Co.).

pieces and then further reduced to $<1/2$ inch with a 4-inch diameter hydraulically driven anvil. The crushed sponge is then screened on a 20-mesh screen. The undersize is recycled to an earlier stage in the process, and the oversize is packed for shipment.

About 90 percent of the raw sponge is recovered as clean, on specification metal. Sponge is packed in polyethylene bags inside $3\frac{1}{2}$ -gallon steel pails at 75 pounds net weight. Each pail is evacuated to 29 inches of Hg, backfilled with argon, and sealed with rubber gasketed lids.

Sampling of the hafnium is done by pressing representative samples of sponge into briquettes from which drillings are taken for spectrographic and chemical analysis. Pressed briquettes are arc melted in an inert atmosphere to buttons from which hardness tests are made, and a nitrogen analysis is made from the lathe turnings from the button.

A typical analysis of sponge produced at the Carborundum Metals Company is shown in Table 3.5.

TABLE 3.5—TYPICAL SPONGE ANALYSIS

(Impurities in ppm)

| Hardness (BHN) | Zr | Al | Cl | Cr | Fe | Mg | Mn | N ₂ | Ni | Pb | Ti | V | O ₂ |
|-------------------|------|----|----|----|-----|-----|----|----------------|-----|-----|-----|-----|--------------------|
| 220--- | 1.5% | 20 | 55 | 80 | 200 | 650 | 15 | 14 | <16 | <16 | <16 | <16 | 1000 to 1200 |

3.3 RECENT DEVELOPMENTS

Desirability of Improved Process

Notwithstanding all precautions taken to prevent contamination by oxygen and nitrogen, it has not been possible to consistently produce, by magnesium reduction, hafnium sponge of high enough purity so that ingots melted directly from the sponge are ductile enough to be satisfactorily forged and rolled. Therefore, most of the hafnium sponge produced to date has been used as feed material for the iodide dissociation process. This process is capable of lowering the oxygen content to levels which permit fabrication from ingots. Lowering the oxygen content by electrorefining in a fused salt bath has been explored experimentally.

Both of these refining processes are expensive, and, as a result, strong efforts are being made to improve the sponge production process to the point where ingots melted directly from the sponge can be fabricated to mill products having suitable mechanical properties. It has been felt until recently that an ingot hardness of 170 BHN or less would be required to accomplish this. In some

cases, however [16, 17], good cold ductility has been obtained on material fabricated from ingots with a hardness of 195 to 200 BHN.

Bi-Metallic Reduction

Recently, considerable effort has been expended in development of a modification of the Kroll process wherein mixtures of sodium and magnesium are used for reduction of zirconium and hafnium tetrachloride [3, 18]. This technique has been referred to as bi-metallic reduction and shows promise of being capable of producing sponge of lower oxygen content and hardness than reduction with magnesium alone.

Molten sodium is easily purified of oxide by filtering in an inert atmosphere leading to a reduction in the total amount of oxygen introduced with the reductant. The use of mixed reductants leads to formation of low melting point salt mixtures which are easily separated from the sponge in the distillation step thus avoiding the difficulties encountered in the removal of sodium chloride when sodium is used alone. Further, since magnesium chloride is reduced by sodium, no free sodium is present in the sponge or residues after distillation as would be the case if no magnesium were present.

Another possible advantage lies in the fact that the mixed salts are less hygroscopic than magnesium chloride so that less moisture is likely to be picked up by any residual chloride in the sponge during handling prior to melting.

Using this technique, the Bureau of Mines has produced sponge with reported oxygen contents as low as 300 ppm and hardnesses below 190 BHN when melted to ingot as compared with oxygen contents of 1,000 to 1,200 ppm and ingot hardnesses of 220 to 240 BHN on sponge produced by magnesium reduction. In view of these favorable results, bi-metallic reduction was being used for all hafnium production at the Bureau of Mines plant at the time it discontinued operation (January 1959).

This process uses the same equipment (with minor modifications) as has already been described for the straight magnesium reduction. In operation, about 550 pounds of tetrachloride is charged into the chloride container and about 78 pounds of magnesium ingot charged into the reduction crucible. After thermal and vacuum treatment of the chloride, as previously described, about 60 pounds of filtered molten sodium is injected into the reduction crucible under pressure of helium from a heated drum.

The sodium line passes through a well in the chloride can to the top of the crucible where a baffle distributes sodium within the

crucible to prevent splashing. After sodium has been added, the lower zone temperature is raised to 725–750° C and the middle zone to 300° C to maintain pressure at 2–3 psi without helium additions. The maximum temperature during the reduction with sodium is 750° C since the vapor pressure of sodium is quite high. At temperatures above 800° C the sodium vapor tends to leave the crucible and react with HfCl_4 in the space between the crucible and the retort, resulting in the formation of hafnium powder and sodium chloride. The material thus formed causes difficulty in crucible removal. The difficulty is amplified if more than 60 pounds of sodium are used with a 55-pound tetrachloride charge. There tends to be a reaction above the surface of the molten sodium which forms excessive vapor phase hafnium which is light and pyrophoric.

If the reaction proceeds too fast, heat generated from the exothermic reaction creates hot spots which cause splashing and overflow of the sodium chloride and magnesium chloride. The reaction of sodium with HfCl_4 is much more exothermic than that of magnesium with HfCl_4 and can be carried out at a lower temperature [18]. The reason heat buildup does not usually accompany the reduction with sodium is that NaCl has a thermal conductivity double that of MgCl_2 , and heat is transferred into the melting of magnesium.

Upon completion of the sodium reaction, the temperature is increased in 25° C increments up to 825–850° C to start the second half of the reduction by magnesium. The purpose of the slow temperature rise is to prevent bursts caused by sodium entrapped in the already formed sponge. A sudden pressure rise is an indication of the presence of free sodium. A 2-hour soak at the end of the magnesium reduction at 875° C is practiced to reduce the pyrophoric nature of the sponge.

Refining of Hafnium Tetrachloride

One of the obvious sources of oxygen and, hence, excessive hardness in hafnium sponge made by metallic reduction of the tetrachloride is the carry-over into the reduction crucible of oxide, oxychloride, water vapor, and other oxygen bearing compounds which may be associated with the tetrachloride.

This carry-over is limited in the normal reduction operations by sublimation, condensation, and resublimation in the process using separate purification and reduction steps. In the P&R-type operation, carry-over is limited by thermal and vacuum treatments followed by a single sublimation step. In either case, gaseous tetra-

chloride is transferred to the reduction crucible leaving behind, in a separate container, most of the impurities which are not volatile at the sublimation temperature of the tetrachloride. Although these techniques are quite effective, complete separation of oxygen bearing compounds from the tetrachloride is not achieved. Improvement in quality of the gaseous tetrachloride reaching the reduction zone would undoubtedly lower the oxygen content and hardness of the sponge.

A number of tests have been conducted in which attempts were made to filter the gaseous tetrachloride prior to reduction [3]. Magnesium turnings, glass wool, zirconium chips, and activated carbon have been used as filtering agents. The materials are placed in a stainless steel basket between the charge can containing HfCl_4 and the water cooled coils on which the tetrachloride is collected. The filters are thought to remove the oxygen bearing compounds from the tetrachloride. Several samples of filtered HfCl_4 subsequently were reduced with magnesium in a separate reduction furnace and arc melted into buttons. The hardnesses of the buttons were 166–238 BHN and average oxygen content was 1,100 ppm. Similar nonfiltered tetrachloride produced buttons with a hardness of 240 BHN and 1,500 ppm of oxygen. Some sponge reduced from filtered HfCl_4 showed an oxygen content as low as 550 ppm.

The most promising technique tried to date is based on the use of anhydrous fused salt mixtures to purify the tetrachloride. This technique was first suggested as a means of producing high purity zirconium tetrachloride [19]. The Wah Chang Corporation currently uses this process.

Hafnium tetrachloride forms low melting eutectics with chlorides of the alkali metals. Such alkali chlorohafnates containing large percentages of hafnium tetrachloride are easily prepared since their melting points are well below the sublimation temperature of hafnium tetrachloride. These salts decompose progressively with increasing temperature to yield a hafnium tetrachloride sublimate of high purity together with an alkali chlorohafnate residue.

For instance, work at the Bureau of Mines [18, 20] indicated a mixture of 19 mol percent NaCl , 19 mol percent KCl , and 62 mol percent HfCl_4 melted at 270–290° C. Upon heating to 600° C, 60 to 70 percent of the contained hafnium tetrachloride was volatilized. The residue chlorohafnate salt was fused with additional hafnium tetrachloride, and, upon reheating to 600° C, 90 to 97 percent of the added tetrachloride was recovered.

A comparison of typical impurity analyses of the tetrachloride before and after fused salt treatment is given in Table 3.6.

TABLE 3.6—FUSED SALT PURIFICATION TESTS [20]

[Typical Spectrographic Analyses of HfCl_4 (ppm)]

| Element | Raw HfCl_4 | Purified HfCl_4 |
|---------|---------------------|--------------------------|
| Cd..... | <0.5 | <0.5 |
| B..... | 10 | <0.2 |
| Al..... | 100 | 40 |
| Fe..... | 3000 | 55 |
| Cu..... | 20 | <10 |
| Pb..... | 25 | <10 |
| Cr..... | 1000 | 40 |
| Si..... | 100 | <20 |
| Mg..... | 275 | 5 |
| Ti..... | 120 | <20 |
| Zn..... | 50 | <50 |
| Ni..... | 200 | 5 |
| Mn..... | 70 | 10 |
| Mo..... | <10 | <10 |
| V..... | <20 | <20 |
| Co..... | <5 | <5 |
| Sn..... | <5 | <5 |
| Zr..... | 1.7% | 1.4% |

The mechanism by which fused salt purification of the tetrachloride takes place is probably threefold. First, during reaction between the alkali chlorides and the HfCl_4 , some volatile impurities such as TiCl_4 , SiCl_4 , and HCl are distilled off; second, other metallic chlorides such as FeCl_3 and AlCl_3 form stable alkali chloride double salts; and third, fine particles of oxide and oxychloride may be physically trapped in the molten bath.

The fused salt purification may be practiced in two general ways: first, as outlined above, by dissolution of the tetrachloride in the salt at low temperature and subsequent sublimation at a higher temperature, and second, by continuously scrubbing the gaseous tetrachloride with a fused salt.

It is not clear which of these techniques gives the best results. It would appear that the alternate dissolution and sublimation might lead to higher purities, whereas continuous scrubbing would be applied more readily to production operations.

Using bi-metallic reduction techniques alone and in combination with fused salt purification of the tetrachloride it has been possible to produce sponge which, when arc melted, could be hot rolled to plate having mechanical properties in the range shown below:

| | |
|--------------------------------|---------------|
| Ultimate tensile strength..... | 75-90,000 psi |
| Yield strength..... | 33-40,000 psi |
| Elongation..... | 17-26% |
| Reduction in area..... | 57-60% |

Consistent production of this quality of sponge would eliminate, for most uses, the necessity for further refining operations prior to melting.

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Chapter 4

REFINING

E. T. HAYES¹ AND D. E. THOMAS,² *Editors*

4.1 INTRODUCTION

Kroll process hafnium sponge, unlike similarly reduced titanium and zirconium, must be further refined to lower its oxygen content before being processed into usable shapes. The need for this step is a result of two factors: (1) hafnium appears to be intrinsically more difficult to fabricate than either titanium or zirconium, and (2) run-of-the-mill hafnium has a higher oxygen content on an atomic basis than does similarly processed titanium or zirconium. Unfortunately, a complete evaluation of these factors has not been made. Normal batch-type Kroll operations produce the three metals of this group with oxygen contents of 0.08–0.1 w/o when scrupulous attention is paid to operating detail. Expressed on an atomic basis, this range of oxygen content becomes 0.24–3.0 a/o in titanium, 0.45–0.57 a/o in zirconium, and 0.94–1.18 a/o in hafnium. When melted to ingot form, such material will have a Brinell hardness of about 100 for titanium, 130 for zirconium, and 190 for hafnium. Titanium and zirconium of this hardness level can be worked either hot or cold without difficulty. Hafnium of this oxygen level and Brinell hardness has borderline ductility; while it can be hot worked to form many objects, its cold ductility is so limited that final sizing operations are difficult.

All hafnium used in nuclear reactors to date has been refined by the iodide decomposition process. This has been done commercially under contract by the Foote Mineral Company, Philadelphia, Pennsylvania, for several years. The current cost for converting Kroll process sponge to iodide crystal bar is about \$11 per pound. There are, accordingly, a number of investigations actively being pursued along the following lines.

- (1) *Improved Sponge Quality*—It is evident that if hafnium sponge with low oxygen content could be routinely produced, it would

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² Westinghouse Atomic Power Division.

be possible to melt the material directly to fabricable ingots. Continuing experimental work on achieving higher purity tetrachloride by the fused salt process at the Bureau of Mines, as described in the preceding chapter, has this as its goal.

- (2) *Alternate Refining Process*—Hafnium sponge may be purified by melting in a high vacuum as in the electron beam melting process. This process, which is being investigated by the Wah Chang Corporation and Temescal Metallurgical Corporation, is described in this chapter. Advances in sponge quality would also contribute to the success of the electron beam melting process.
- (3) *Alternate Reduction Process*—Electrorefining offers the possibility of supplanting both the Kroll process and the de Boer process. This approach, described in this chapter, is being taken by the Bureau of Mines (Boulder City).
- (4) *Low Cost de Boer Process Feed Material*—A cooperative program between the Bureau of Mines (Albany) and the Foote Mineral Company is designed to develop a substitute feed material for the iodide process. This approach is discussed briefly in this chapter.

With the exception of the fused salt process for tetrachloride purification, the work outlined above is in fairly preliminary stages, and it is expected that developments will appear quite rapidly.

4.2 THE IODIDE PROCESS

By E. M. Sherwood³ and I. E. Campbell⁴

The iodide-refining process, suggested by van Arkel and de Boer [1] in 1925, is now widely recognized as an effective method for preparing a number of high-purity metals. Although some reduction in metallic impurities is frequently obtained, the iodide process is primarily used because of its effectiveness in producing metal low in nonmetallics and, more particularly, low in nitrogen, oxygen, and carbon.

Iodide refining of hafnium has been performed for the Atomic Energy Commission since 1952 by a single supplier, the Foote Mineral Company. However, the details of the process are considered to be proprietary, so that no discussion of the process as commercially practiced is presented here. In 1951, over 500 pounds of hafnium crystal bar was produced at the Bettis Plant of the Westinghouse Electric Corporation by Shapiro [2] for use in the land-based prototype of the *Nautilus* reactor. The fact that this was rather easily done in equipment originally designed for iodide refining of zir-

³ Battelle Memorial Institute.

⁴ National Steel Corporation.

conium, together with other published information makes it possible to delineate the main features of the iodide process for refining hafnium. Many of the details of the process depend upon the design of the particular equipment being used.

The basic principles of the van Arkel-de Boer process have been discussed extensively in previous publications (e.g., Ref. 3) and need not be reviewed in detail here. Suffice it to say that a bithermal, closed-cycle system is employed in which the metal iodide can be simultaneously synthesized and decomposed. Volatile iodides are formed by reaction of iodine vapor with a crude metal feed at the lower temperature, and the iodides thus formed are subsequently thermally dissociated, on a suitable deposition surface, at the higher temperature. A resistively heated wire or rod is normally used as the deposition surface, but other means of heating and other types of surfaces may, in principle, be employed. The iodide process is particularly effective with those metals which do not form volatile oxides or oxyiodides.

The van Arkel-de Boer process has been used for the commercial production of titanium, zirconium, and thorium, and an improved iodide-refining process is now being used for the production of ultra-pure chromium metal. Although a number of other metals have been prepared experimentally via the iodide process, none of these has been produced on a commercial scale.

The original van Arkel-de Boer synthesis, which is a closed-cycle process, leaves much to be desired as a commercial method for the production of low-cost metals, and consideration has been given to the development of semi-continuous processes employing low-cost feed materials. Although considerable progress has been made in this direction experimentally, no continuous iodide process has been utilized commercially for the production of metal.

Several laboratories are known to have been working on the development of a semi-continuous process for the production of transistor-grade silicon with promising results. However, at the present time, the prospects of producing other than premium-grade materials by a semi-continuous iodide process do not appear attractive. It would seem more likely that further progress in the commercialization of iodide processes will involve improvements in the closed-cycle process rather than development of new semi-continuous processes.

As would be anticipated on the basis of the marked similarity of the chemistry of hafnium and zirconium, the conditions for the preparation of these two metals are quite similar—so much so, in fact, that much of the experimental work in the preparation of iodide hafnium has been carried out in equipment initially constructed for the preparation of zirconium. The similarity is also

suggested by the fact that in the iodide process for zirconium purification, the hafnium content of the crystal bar is identical to that of the feed material [3].

Background Information

Information available on the iodides of hafnium is quite limited. Table 4.1 is a compilation of values for some of the physical and thermodynamic properties of HfI_4 . Owing to the scarcity of experimental data, many of the values were estimated from theoretical considerations.

Although, in many respects, hafnium is quite similar to zirconium chemically, the lower oxidation states of hafnium appear to be less stable than those of zirconium. This has been attributed [4] to two factors: (1) the higher heat of sublimation of hafnium, which tends to make the lower state more readily disproportionate, and (2) an ionization potential factor.

The difference in the ease of reduction of the tetrahalides of hafnium and zirconium is the basis of a proposed process [5] for the separation of zirconium and hafnium. In this process, zirconium tetraiodide is preferentially reduced by zirconium powder to the tri-iodide, and the hafnium iodide is then selectively volatilized from the mixed iodides. Although some interest has been evinced in the commercial feasibility of the process, there is no evidence at present to indicate that it offers any advantage over existing processes (see Chap. 2).

Details of the Iodide Process for Hafnium

Feed Material

Iodide hafnium can be prepared from various types of metallic feed materials. However, magnesium-reduced "hafnium sponge" is most commonly employed [6-9].

Since some metallic impurities are transferred in the iodide process, a feed which is low in metallic impurities, particularly those forming volatile iodides of intermediate stability, is desirable. Table 4.2 contains published analytical data on several types of hafnium sponge. Of the impurities listed, zirconium, iron, silicon, and possibly aluminum are the most likely to transfer in the iodide process under the conditions employed in hafnium refining. However, some refinement with respect to iron, silicon, and aluminum is usually obtained.

The feed material is usually conditioned for use [10] by washing, vacuum drying, and outgassing. For best results, it is desirable to

outgas the feed at a temperature somewhat above that reached during deposition. Outgassing should be carried out in the deposition vessel to avoid excessive handling. The feasibility of developing lower cost feed material is being studied by a commercial supplier in cooperation with the U.S. Bureau of Mines. In the process under investigation, a mixture of hafnium oxide and carbon is arc melted. The resultant ingot, consisting of hafnium metal and hafnium carbide, is crushed and blended with hafnium sponge so that the over-all carbon content is about 1 percent. This mixture can then be fed to the iodide decomposition units. No further details are available.

Deposition Equipment

The deposition vessel used in laboratory experiments may be constructed of Pyrex glass or Vycor (see Figs. 4.1 and 4.2). In commercial practice, the deposition vessel is constructed of heat resistant metals. The material used in the *Nautilus* prototype was produced in the equipment illustrated schematically in Figure 4.3. This equipment, which had originally been built for the purpose of conducting experiments on the iodide process for zirconium, utilizes a Hastelloy-B vessel and a molybdenum feed retainer. The reaction vessel is heated externally by means of a salt bath. Hollow, water cooled electrodes with molybdenum tips are employed to supply heating current to the crystal bar during deposition [13]. The equipment used by the present commercial supplier in producing zirconium crystal bar has been described in the literature [3]. The reaction vessels were 9 inches in diameter and 24 inches long and were constructed of Inconel. It is believed that similar equipment, with improved vessel head design to minimize leaks, is being used for hafnium purification.

To control the temperature of the resistively heated deposition elements, a variable, low-voltage/high-current power supply is required. This can be made automatic, but the automatic equipment so far employed is complicated and expensive; hence, manual control is generally used.

The vacuum system is provided with refrigerated traps to remove any undecomposed iodide so that pump contamination and corrosion can be avoided. In the classical van Arkel-de Boer process the deposition vessel is sealed off from the vacuum system during deposition; however, it has been found desirable, in small-scale operation at least [14], to evacuate the vessel either intermittently or continuously during deposition. This minimizes the accumulation of gases (principally hydrogen) and the consequent slowing down of deposition.

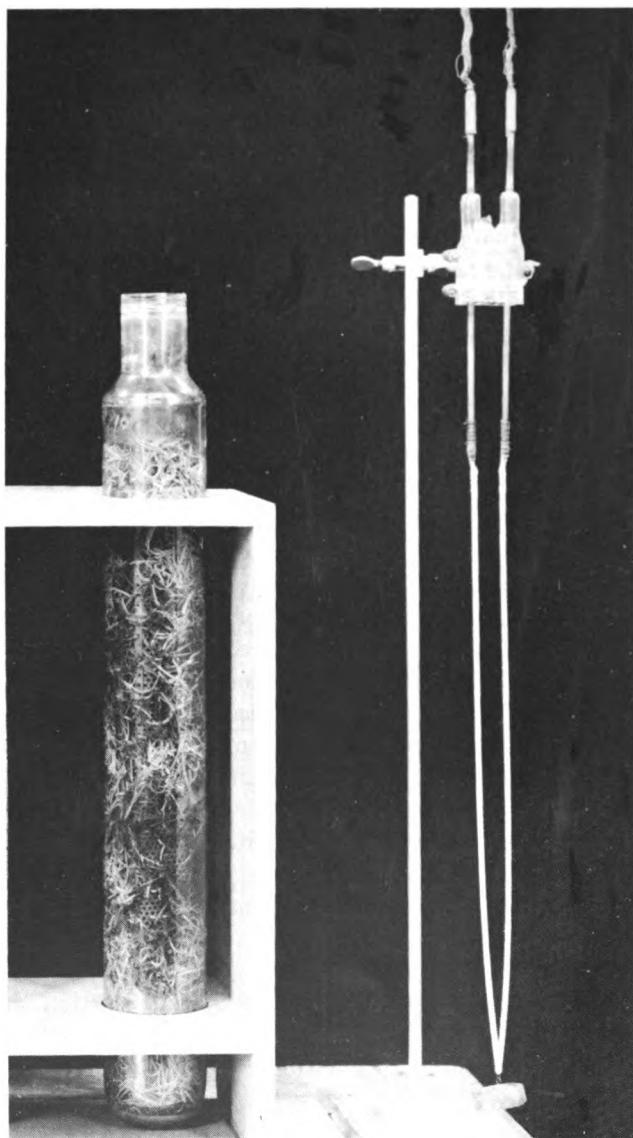


FIGURE 4.1. Laboratory-Scale Deposition Unit (from *The Metal Thorium*, H. A. Wilhelm, ed., American Society of Metals, Cleveland, 1958).

For more detailed descriptions of deposition equipment, the reader is referred to Chapter 5 in *The Metallurgy of Zirconium* [3].

Procedure

The procedures employed in the preparation of hafnium crystal bar are similar to those employed in the preparation of iodide zirconium.

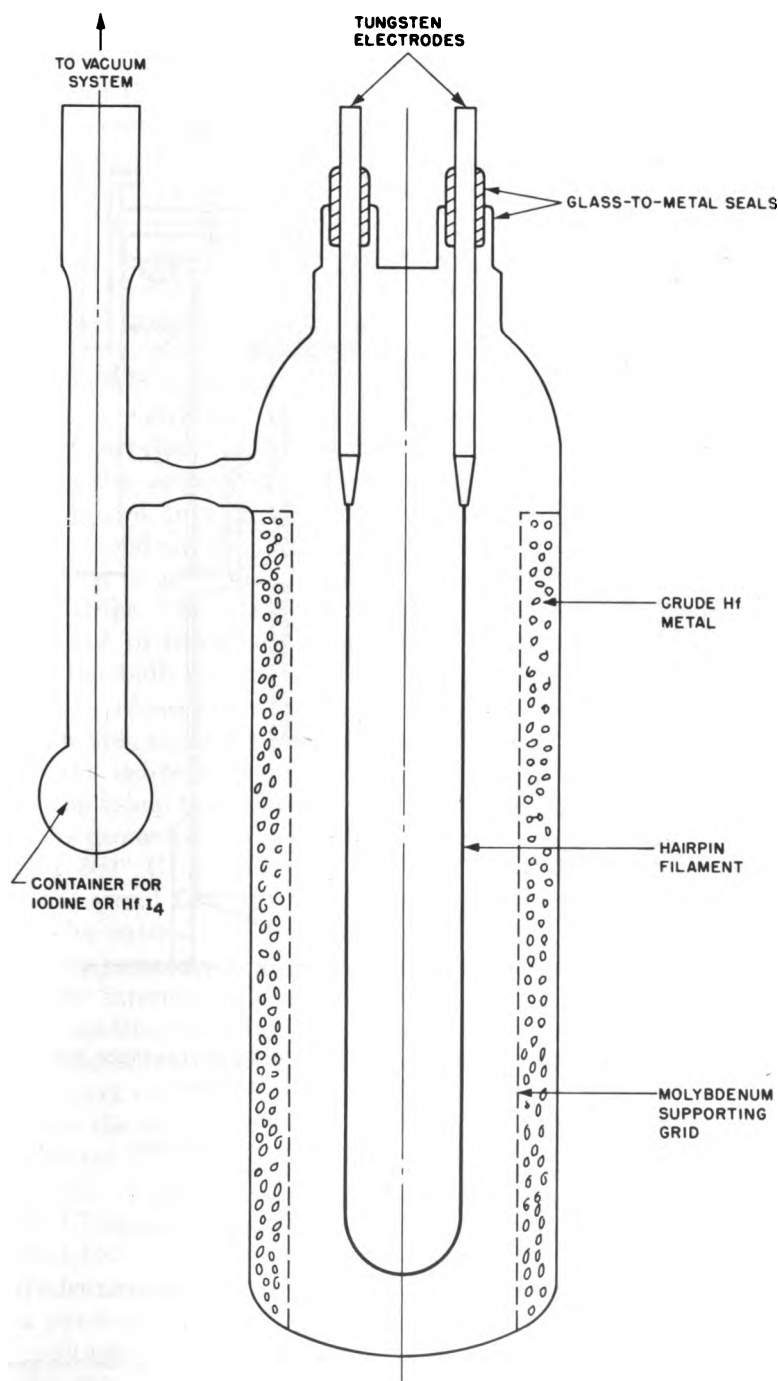
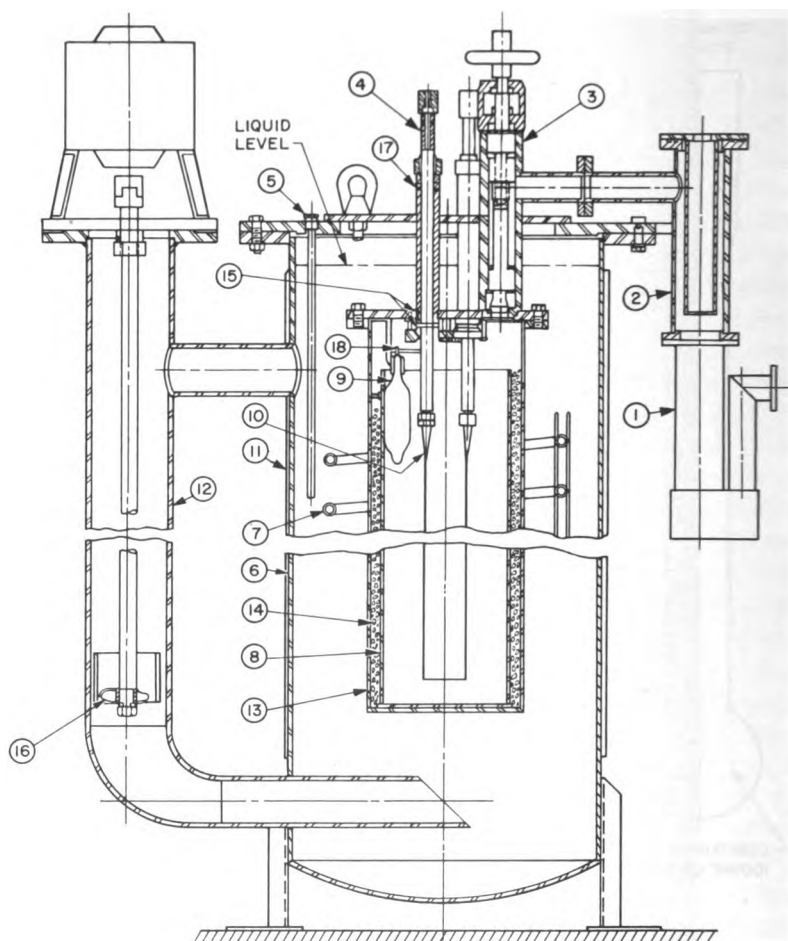


FIGURE 4.2. Glass Deposition Vessel (from USAEC—*The Metallurgy of Zirconium*, B. Lustman and F. Kerze, Jr., eds., McGraw-Hill, New York, 1955).



- | | |
|-------------------------|---|
| 1 HIGH-VACUUM PUMP | 10 MOLYBDENUM ELECTRODE TIP |
| 2 COLD TRAP | 11 STRIP HEATERS |
| 3 NON-RISING STEM VALVE | 12 CIRCULATOR |
| 4 COPPER ELECTRODE | 13 HASTELLOY B VESSEL |
| 5 THERMOCOUPLE | 14 HAFNIUM SPONGE |
| 6 IMMERSION TANK | 15 CERAMIC BUSHINGS |
| 7 COOLING COIL | 16 AGITATOR WITH SHROUD |
| 8 MOLYBDENUM SCREEN | 17 O-RING SEAL |
| 9 HfI_4 BOTTLE | 18 Hf WIRE HOLDING BOTTLE (9) IN PLACE |

FIGURE 4.3. Deposition Unit (from USAEC—*The Metallurgy of Zirconium*, B. Lustman and F. Kerze, Jr., eds., McGraw-Hill, New York, 1955).

Although there are advantages to conditioning the feed prior to its introduction into the deposition bulb, it is usually handled wet because of the safety hazard involved and then conditioned in place with makeup metal being added before the unit is sealed. The initial filament, a hafnium wire, is attached to the electrodes which are a part of the head of the deposition vessel.

After the residual feed is washed and makeup feed is added as required, the unit is assembled and evacuated at room temperature until the feed is essentially dry except for adsorbed moisture. The vessel is then heated slowly under vacuum to the desired outgassing temperature, preferably somewhat above the desired deposition temperature, and is outgassed for a period of several hours. In many cases, it is convenient to schedule operations so that the vessel can be outgassed overnight.

When the outgassing is completed, iodine or hafnium tetraiodide is introduced into the bulb. In metal equipment, an ampule of iodine or iodide may be broken open in the vessel. Commercial practice is to add iodine crystals to the deposition vessel through a seal-off tube. In glass or Vycor equipment, it is usually more convenient to introduce iodine vapor by "flaming" an ampule between the bulb and the vacuum line. To avoid excessive loss of iodine, a constriction is provided between the ampule and the vacuum line, and the constriction is chilled to form a plug of iodine while the iodine is being added to the system.

The optimum bulb temperature will depend upon the feed employed and the geometry of the system, but a bulb temperature of approximately 300°C is usually employed. It should be noted, however, that the actual feed temperatures are frequently substantially higher than the external bulb temperature which is normally recorded. Feed temperatures may, for example, be as much as 500°C higher than the external wall temperature. For a discussion of the effect of the tendency of tetra-iodides to react with metal to form tri- and di-iodides at optimum deposition temperatures, the reader is referred to the work of Fast [15].

When the bulb is at the desired deposition temperature, deposition is initiated by heating the hafnium wire filament to approximately $1,600^{\circ}\text{C}$. (Some investigators prefer a temperature of as high as $1,700$ – $1,750^{\circ}\text{C}$ while others prefer a somewhat lower temperature of $1,300$ – $1,400^{\circ}\text{C}$.⁵) The filament temperature is maintained at the desired value by periodic reductions in the applied voltage usually by a predetermined schedule. During the early stages of deposition the voltage may be adjusted to maintain the product of the cube

⁵ It is interesting to note that hafnium is close packed hexagonal at the deposition temperature, whereas zirconium is body-centered cubic. Further study of the influence of the crystal structure of the metal upon the growth rate and form of the rod would be enlightening.

root of the current times the voltage constant ($I^2E = K$). However, this relationship does not hold as deposition progresses.

The unit may be sealed off from the vacuum system during deposition or may be continuously evacuated through a porous plug of condensed iodide. In the latter case, it is usually desirable to flame the plug at suitable intervals to prevent it from becoming too effective a seal.

When the crystal bar reaches the desired size, as determined by the current-voltage relationship, the filament power is shut off, the vessel is cooled, and an inert gas is bled in before the vessel is opened to air.

Both the crystal bar and the feed are washed to remove residual iodides. As in the case of all iodide metals, care must be taken to remove any condensed iodide from the surface of hafnium crystal bar immediately after its removal from the deposition vessel, since the oxides which form on exposure to atmospheric moisture present a potential source of contamination of the deposited metal.

Hafnium is somewhat easier to deposit by the iodide process than zirconium [2] by virtue of its higher melting point, lesser tendency to alloy with molybdenum (both of which tend to decrease the probability of burnouts), and its lower tendency to creep while hot.

Rate of Deposition

The deposition rate varies markedly with the feed material and operating conditions. In small Pyrex units of the type shown in Figure 4.1, average deposition rates of approximately 9 g/hr/ft were

TABLE 4.1—THERMODYNAMIC, FUSION, AND VAPORIZATION DATA FOR HfI_4 and ZrI_4

| | HfI_4 | ZrI_4 |
|---|----------------------------|---------------------|
| Heat content at 500° K, ($H_T = H_{298}$), kcal/mole ¹ .. | 7.1 ($\pm 5\%$) | 7.1 ($\pm 5\%$) |
| Entropy increment at 500° K, ($S_T = S_{298}$), cal/° K ¹ .. | 18.2 ($\pm 5\%$) | 18.2 ($\pm 5\%$) |
| Free-energy at 298° K, $-(F - H_{298})/T$, cal/mole/° K ¹ .. | 64.5 ± 2 | 63.4 ± 2 |
| at 500° K ¹ .. | 68.5 ± 2 | 67.4 ± 2 |
| Free-energy function at 298° K, $(\Delta F - \Delta H_{298})/T$, cal/° K ¹ .. | 70.9 | 70.4 |
| at 500° K ¹ .. | 69.6 | 69.1 |
| Heat of formation, ΔH_{298} , Kcal/mole ² .. | ³ -175 ± 30 | -160 ± 20 |
| Melting point, T_M , ° K ² .. | ³ 750 | 772 |
| Heat of fusion, ΔH_M , cal/mole ² .. | ³ 11,000 | ³ 11,500 |
| Entropy of fusion, ΔS_M , cal/mole/° K ² .. | 15 | 15 |
| Temperature at which partial pressure = 10^{-4} atm, ° K ² .. | ³ 475 ± 10 | 495 |
| = 1 atm, ° K ² .. | ³ 700 | 704 |
| Heat of sublimation, ΔH_V , cal/mole ² .. | ³ 28,000 | 29,030 |
| Entropy of sublimation, ΔS_V , cal/mole/° K ² .. | 40 | 41.2 |

¹ Values for HfI_4 from Chap. 9; values for ZrI_4 from K. K. Kelley, private communication.

² Brewer, Ref. 4.

³ Estimated values.

TABLE 4.2—ANALYSES OF HAFNIUM SPONGE

| REDUCED WITH Mg [4] | | BOMB REDUCED WITH Ca, I ₂ BOOSTER [7] | | BOMB REDUCED WITH Ca [8] | | KROLL PROCESS [9] | |
|-----------------------|-------------------|---|-------------------|-----------------------------|-------------------|----------------------|-------------------|
| Element | Composition (w/o) | Element | Composition (w/o) | Element | Composition (w/o) | Element | Composition (w/o) |
| Al..... | 0.010-0.505 | Al..... | 0.04 | C..... | 0.07 | Al..... | 0.003 -0.005 |
| Ca..... | <0.003 | B..... | 0.001 | Ca..... | <0.01 | Cl..... | 0.010 -0.020 |
| Cu..... | 0.001-0.014 | Ba..... | <0.01 | Fe..... | <0.01 | Co..... | 0.001 |
| Fe..... | <0.003-0.082 | Be..... | <0.000002 | Mg..... | <0.01 | Cr..... | 0.0005-0.01 |
| Hf ¹ | 98.38 -99.07 | Ca..... | 0.03 | N..... | 0.05 | Cu..... | 0.005 -0.01 |
| Mg..... | <0.003-0.057 | Cd..... | <0.0002 | O..... | Not determined | Fe..... | 0.04 |
| Ni..... | <0.003-0.007 | Co..... | <0.001 | Si..... | <0.01 | Mn..... | 0.003 |
| Si..... | <0.003-0.023 | Cr..... | <0.001 | Zn..... | <0.002 | Mo..... | 0.001 |
| Zr..... | 0.85 -1.59 | Cu..... | <0.002 | Zr..... | <0.01 | N ₂ | 0.001 -0.003 |
| | | Fe..... | 0.02 | | | Ni..... | 0.0005 |
| | | Li..... | <0.01 | | | O ₂ | 0.065 -0.095 |
| | | Mg..... | 0.01 | | | Pb..... | 0.002 -0.003 |
| | | Mn..... | 0.001 | | | Si..... | 0.002 -0.010 |
| | | Mo..... | 0.001 | | | Ti..... | 0.005 |
| | | Na..... | <0.01 | | | V..... | 0.002 |
| | | Ni..... | 0.001 | | | Zn..... | 0.0005-0.005 |
| | | P..... | <0.01 | | | | |
| | | Pb..... | 0.001 | | | Zr/(Hf+Zr) | 1.3 -1.4% |
| | | Si..... | 0.01 | | | | |
| | | Sn..... | <0.001 | | | | |
| | | Ti..... | 0.0004 | | | | |
| | | V..... | 0.001 | | | | |
| | | Zn..... | <0.01 | | | | |
| | | (Hf/Zr=98/2) | | | | | |

¹ By difference excluding O₂, N₂, and H₂ which were unknown.

obtained in the preparation of crystal bar approximately $\frac{1}{4}$ inch in diameter.

In the limited production work carried out in metal units of the type shown in Figure 4.3, average deposition rates of approximately 22 g/hr/ft were obtained.

The rate of deposition increases to a greater extent as the run progresses in the case of hafnium deposition than it does in the case of zirconium deposition; hence, higher average rates are obtained when larger diameter bars are prepared [2].

The largest hafnium crystal bar reported to date was 1.375 inch in diameter. Usually, bars of 0.5 to 0.75 inch in diameter are produced.

Purity of the Product

The purity of iodide hafnium is comparable with that of other iodide metals. It is dependent, of course, on the purity of the feed material as has already been noted. Analyses of three lots of iodide

hafnium are shown in Table 4.3. Material C was reported to be the highest purity iodide hafnium produced prior to 1956 [16].

Unfortunately, no definitive data are available which give a complete analysis of hafnium crystal bar and of the feed from which it was produced; hence, no direct experimental values can be cited for the degree of refining obtained. However, Table 4.4, which presents typical sponge and typical arc-melted crystal bar analyses, should provide a reasonably good basis for comparison. Effective reduction in chromium, magnesium, oxygen, and possibly iron is indicated.

TABLE 4.3—ANALYSES OF IODIDE HAFNIUM

| Element | Material A[15] (ppm) | Material B[6] (ppm) | Material C[10] (ppm) |
|----------------------|-------------------------|------------------------|-------------------------|
| Al..... | 40 | 660 | 20 |
| C..... | 200 | (¹) | (¹) |
| Ca..... | 50 | 110 | (¹) |
| Cr..... | 30 | (¹) | <30 |
| Cu..... | 8 | 40 | 40 |
| Fe..... | 200 | <30 | 800 |
| Mg..... | 10 | 80 | 40 |
| Mn..... | 10 | (¹) | (¹) |
| Mo..... | 10 | (¹) | 60 |
| N ₂ | 10 | 40 | (¹) |
| Ni..... | 10 | 80 | 40 |
| O ₂ | (¹) | 370 | 120 |
| Pb..... | 10 | (¹) | (¹) |
| Si..... | 60 | 340 | 150 |
| Sn..... | 10 | (¹) | (¹) |
| Ti..... | 20 | <30 | 100 |
| V..... | (¹) | (¹) | 40 |
| Zr..... | 20, 000 | 7, 800 | 80 |

¹ Not reported.

TABLE 4.4—TYPICAL ANALYSES FOR KROLL PROCESS SPONGE AND ARC-MELTED IODIDE CRYSTAL BAR

| | Concentration (ppm) | |
|----------------------|--------------------------------------|---|
| | Kroll Process Sponge ¹ | Arc-Melted Iodide Crystal Bar ² |
| Al..... | 20 | 50 |
| Ce..... | 55 | (Not determined) |
| Cr..... | 80 | <10 |
| Fe..... | 200 | 100 |
| Mg..... | 650 | <10 |
| Mn..... | 15 | <10 |
| N ₂ | 14 | 20 |
| Ni..... | <16 | <10 |
| Pb..... | <16 | <10 |
| Ti..... | <16 | <10 |
| V..... | <16 | (Not determined) |
| O ₂ | 1000-1200 | 500 |

¹ Produced at Carborundum Metals Co. (see Chap. 3).

² See Chap. 5.

4.3 ELECTROREFINING

By D. Baker ⁶

Over the past century the production and refining of metals through the application of electrochemical techniques has increased markedly, especially in the application and use of these techniques in fused salts. Charles Martin Hall and Paul L. T. Heroult, almost simultaneously, on opposite sides of the Atlantic, discovered that aluminum oxide could be dissolved in molten cryolite and that the dissolved oxide could be reduced electrolytically to produce metallic aluminum. The Hall-Heroult process, basically the same today as when discovered in 1886, is an electrochemical production technique which has grown into a major industry. From the 1880's to the present day, researchers have studied and applied molten salt electrochemical techniques to various metals of the periodic table. W. J. Kroll, in his paper "The Fused Salt Electrolysis for the Production of Metal Powders," presented to the Symposium of Electrometallurgy, Pacific Northwest Section meeting, May 1945, gave an extensive review of this literature. In recent years the technical feasibility, if not the economical and operational feasibility, of fused salt electrorefining of titanium has been shown by many researchers [18-25].

General Considerations

In developing a research program to establish the optimum conditions for recovering high-purity hafnium metal from off-grade sponge and fabrication scrap, the development of an electrolyte was the first consideration. The electrolyte selected has to be free of elements such as oxygen, with which hafnium reacts readily, and maintain stability at operating temperatures. Also, since some of the deposits were leached to remove occluded salts, which in most instances is preferable to vacuum distillation, it was desirable to select an electrolyte that could be removed from the leach solution in an anhydrous form or was sufficiently cheap to permit discarding. These considerations narrowed the possible salts to the halides, and solubilities or economics further narrowed the field to the chlorides. Of the single salts, sodium chloride best met the requirements, but the temperature of cell operation had to be sufficiently high to fuse it (801° C). The operational temperature was lowered by using mixed salts such as potassium chloride, lithium chloride, and/or sodium chloride to form eutectic mixtures, but the addition of another salt increased further the possibility of introduction of impurities.

⁶ U.S. Bureau of Mines.

The electrolyte selected and the required temperature of operation define the materials of construction used in the cell. The problem of handling hot corrosive gases in electrorefining does not exist because none are liberated. Therefore, in most instances, common construction materials such as iron can be used throughout the cell. An essential design factor in cell construction is that the cell be airtight to allow complete internal blanketing with an inert atmosphere such as helium or argon. This blanketing protects the electrolyte from gaseous contamination and protects the deposits from the time they are removed from the electrolyte until they are cooled to room temperature.

The U.S. Bureau of Mines Electrometallurgical Experimental Station at Boulder City, Nev., has, under a program supported by the Atomic Energy Commission, undertaken development research to ascertain the feasibility of applying fused salt electrorefining techniques to hafnium scrap. The program, at this writing, has consisted of a series of preliminary examinations to ascertain whether hafnium scrap can be recovered in a purified state by this technique and which electrolytes offer optimum purification and ease of operation. This section, therefore, is a progress report which answers only the initial question of whether hafnium can be purified by the fused salt electrorefining technique. The basic premise of this program has been to develop an electrolyte and the operational technique necessary to produce high-purity hafnium metal from off-grade sponge and fabrication scrap.

Equipment

Electrolyte development experiments were performed in a group of 12-inch diameter laboratory cells shown schematically in Figure 4.4. These cells were constructed from a 30-inch piece of 12-inch diameter iron pipe. The bottom of the cell was sealed by welding in a section of 1/2-inch iron plate, and the top of the cell section was equipped with a water-cooled flange to which the rubber gasketed lid could be bolted. The lid was equipped with two 4-inch diameter openings to which receiver chambers could be attached and an additional opening for the circulation of the inert gas and the measurement of temperature and pressures within the cell. The receiver sections consisted of a 4-inch water-cooled slide valve and a 15-inch long, water-cooled chamber for cooling deposits before exposure to the atmosphere. The slide valve sealed the cell proper from the atmosphere during recovery of the deposits. The cells were assembled and thoroughly checked for leaks under both vacuum and pressure.

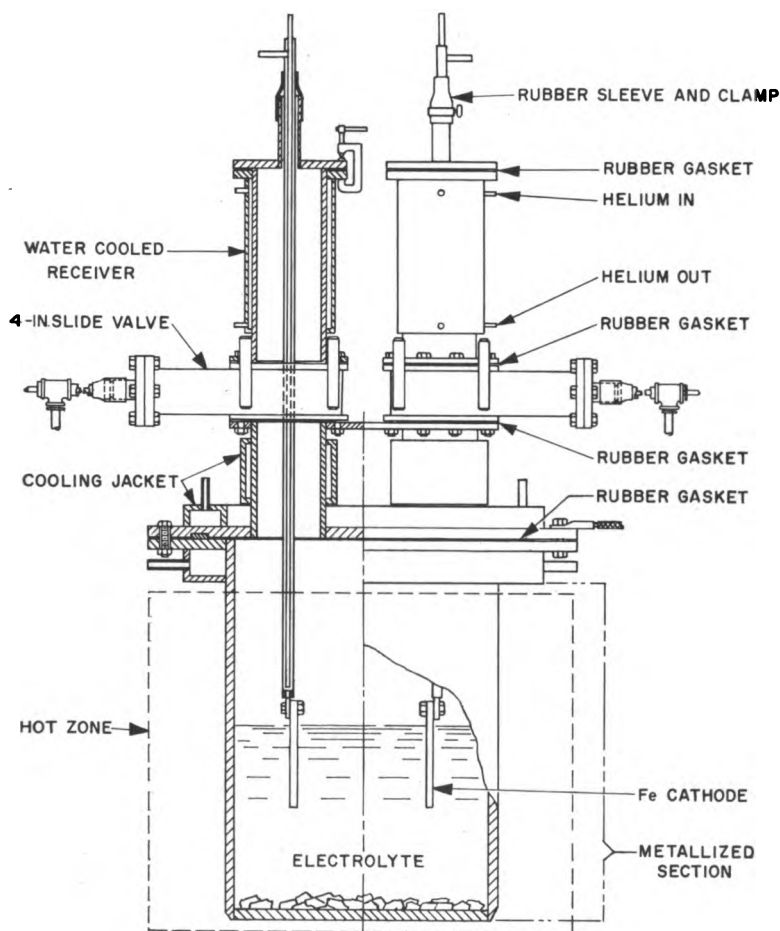


FIGURE 4.4. Twelve-In. Diameter Cell Used in Hafnium Fused Salt Electrorefining Tests.

Investigations

Electrolytes examined during the first nine months of the program consisted of mixtures of sodium chloride, potassium fluohafnate, potassium-lithium chloride, and sodium-potassium chlorides as well as unmixed sodium chloride. With the one exception (when potassium fluohafnate was used), the hafnium-carrying ions were added to the electrolyte either by subliming hafnium tetrachloride through hafnium metal beneath the bath or by direct chlorination of hafnium metal in the bath.

This technique, when used in preparing the initial electrolytes for the titanium investigation, had produced subchlorides of titanium in the baths, but if subchlorides of hafnium were formed they were not

stable. A reaction between HfCl_4 and hafnium took place, but when samples of the electrolyte were taken there appeared to be a disproportionation of reaction product on cooling which left an extremely fine hafnium metal and hafnium tetrachloride. This disproportionation is exemplified by the equation $2\text{HfCl}_2 \rightleftharpoons \text{Hf} + \text{HfCl}_4$. Operation of electrolytes which essentially contained only sodium chloride and hafnium chloride as carrier ions were difficult to stabilize with respect to the soluble hafnium content because the hafnium chloride sublimed to the colder sections of the cell as hafnium tetrachloride. Addition of a second salt such as potassium chloride or lithium chloride greatly alleviated this difficulty even when comparable temperatures of cell operation were used.

Table 4.5 presents a summation of the pertinent conditions under which each of the electrolytes was studied.

The material used as an anode feed consisted of fines screened from Kroll hafnium sponge production. Material arc-melted from these fines had hardnesses ranging from 268 to 323 BHN and contained the following weight percentages of impurities: Si—0.01; Mg—0.125; Mn—0.056; Fe—0.005; Cr—0.08; Al—0.04; Cu—0.05; and O_2 —0.175.

TABLE 4.5—SUMMATION OF ELECTROLYTE STUDIES

| ELECTROLYTE COM- POSITION, SALT | SOL HF (%) | AVE. OPER. TEMP. (° C) | INITIAL CATH- ODE CURRENT DENSITY (amp/sq ft) | | RECTI- FIER VOLT- AGE | TYPE OF DEPOSIT | BHN | |
|--|------------------|---------------------------------|--|------|--------------------------------|----------------------|------|------|
| | | | Min. | Max. | | | Ave. | Best |
| NaCl..... | 3.0 | 830 | 70 | 560 | 0.7 | Slimes..... | | |
| NaCl..... | 8.0 | 850 | 70 | 560 | 0.6 | Fine Crystals..... | 200 | 181 |
| 45% NaCl-55% KCl..... | 8.7 | 750 | 175 | 225 | 0.75 | Coarse Crystals..... | 190 | 185 |
| 45% NaCl-55% KCl..... | 4.5 | 700 | 70 | 250 | 0.5 | Dense Plate..... | 183 | 173 |
| 45% NaCl-55% KCl..... | 4.7 | 700 | 500 | 650 | 0.75 | Coarse Crystals..... | 190 | 185 |
| 45% NaCl-55% KCl..... | 4.7 | 940 | 75 | 250 | 0.6 | Coarse Crystals..... | 192 | 182 |
| 95% NaCl-5% KCl..... | 5.1 | 840 | 70 | 500 | 0.3 | Coarse Crystals..... | 158 | 139 |
| 55% KCl-45% LiCl..... | 4.2 | 440 | 75 | 250 | 4.0 | Fine Crystals..... | | |
| NaCl-K ₂ HfF ₆ | 5.1 | 850 | 150 | 300 | 0.5 | Medium Crystals..... | 205 | 187 |

Although the major criterion used for evaluation of the cathode deposits was hardness, a few of the deposits were chemically analyzed. A typical analysis of these deposits is as follows: Fe—0.001; Si—0.010; Mg—0.009; V—0.001; Cr—<0.001; Mn—0.015; O_2 —0.039; Cu—0.034; and Na—<0.005.

The deposit shown in Figure 4.5 was produced at an initial cathode current density of 175 amp/sq ft in the seventh electrolyte, as tabulated in Table 4.5. Figure 4.6 shows a cylindrical iron cathode and

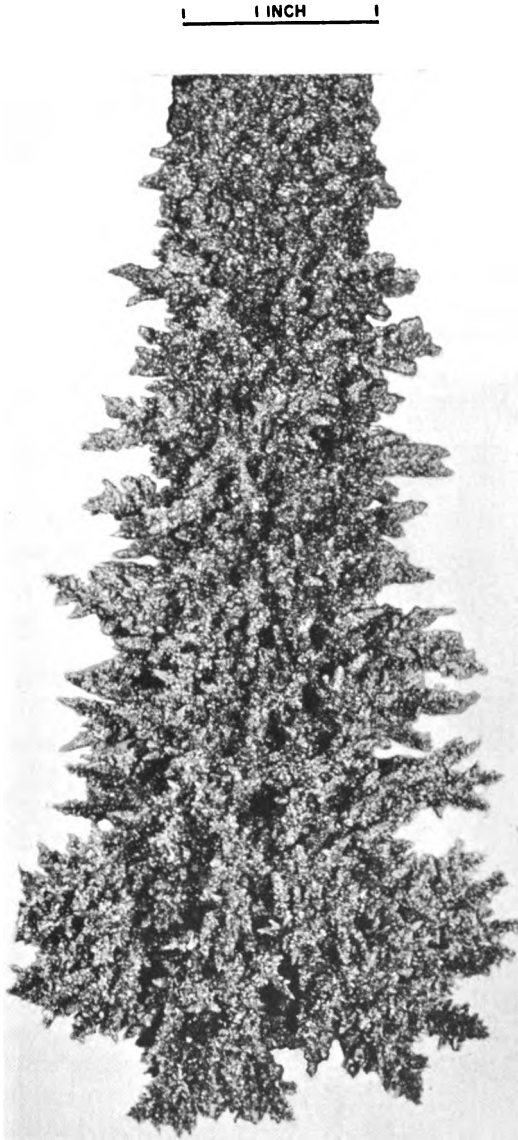


FIGURE 4.5. High Purity Hafnium Cathode Deposit from 95 Percent NaCl-5 Percent KCl Electrolyte.

the plate deposit produced on it in the fourth electrolyte at an initial cathode current density of 150 amp/sq ft.

Data on two typical deposits produced on an iron cathode in the electrolyte consisting of essentially sodium chloride (93-95 percent)

with only a minor amount of potassium chloride (5–8 percent) are as follows:

| RUN | INITIAL CATH- ODE CURRENT DENSITY (amp/sq ft) | CURRENT EFFICIENCIES ¹ (%) | AVERAGE RECTIFIER VOLTS | METAL RECOVERED (g) | BHN |
|---------|--|---|-------------------------------|---------------------------|-----|
| A ----- | 177 | 85.5 | 0.28 | 358 | 148 |
| B ----- | 177 | 92.8 | 0.30 | 533 | 158 |

¹ Based on Hf valence of four.

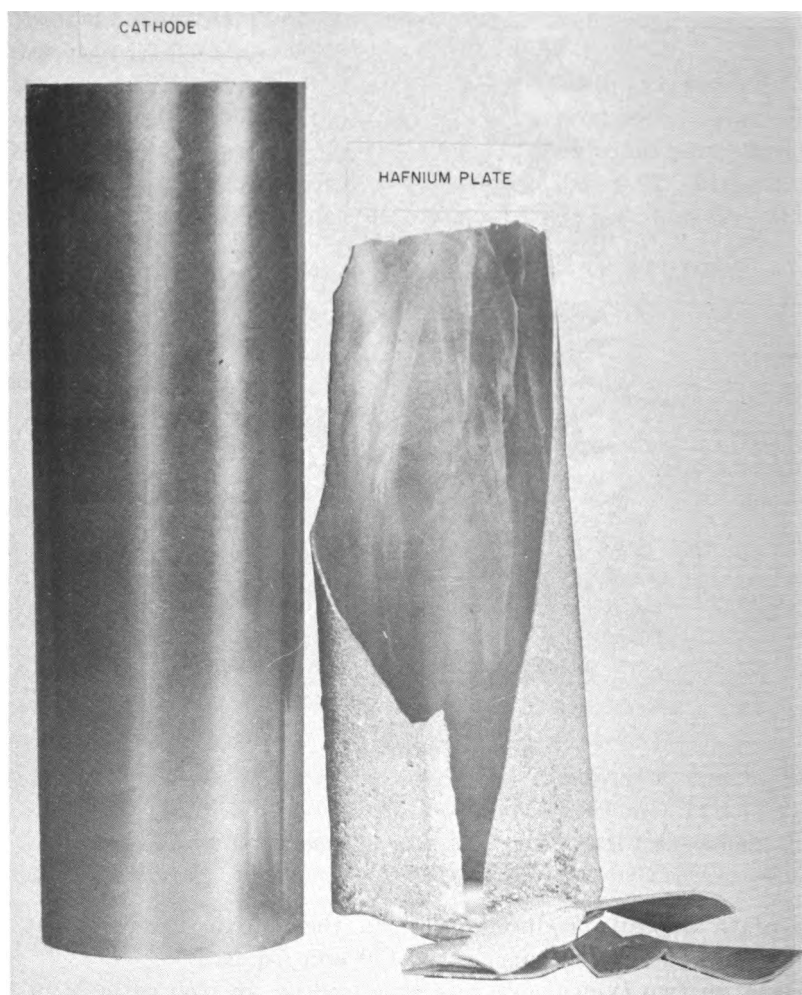


FIGURE 4.6. Cathode and Hafnium Plate Produced in 45 Percent NaCl-55 Percent KCl Electrolyte.

A hardness evaluation of deposit A was made without sizing. Deposit B was sized, and the screen analysis showed 91.5 percent of +28 mesh, 6.6 percent of -28 +48 mesh, and 1.9 percent of -48 mesh.

Deposits such as these, while still adhering to the cathode, are given a preliminary leach with water to which has been added 5 percent HCl by volume. The deposits are then scraped from the cathode, chopped in a mechanical, high speed liquid blender, given a second leach, washed with distilled water until free of chloride ion, and then washed with alcohol and dried. The dried hafnium is then normally sized by screening into three fractions, +28, -28 +48, and -48 mesh, and samples are taken for hardness and chemical evaluation from those fractions of sufficient size.

At this time it can be said that the refining of hafnium scrap can be accomplished by the fused salt electrolyrefining technique; however, the degree of purification and the optimum electrolyte and operational techniques still need to be determined.

4.4 ELECTRON BEAM PROCESS FOR THE PURIFICATION AND CONSOLIDATION OF HAFNIUM

By C. d'A. Hunt,⁷ H. R. Smith, Jr.,⁷ C. W. Hanks,⁷ and E. F. Baroch⁸

The direct consolidation of hafnium sponge metal into reactor grade ingot without intermediate and separate purification steps has been investigated for several years. For zirconium, this direct processing of sponge into ingot was successfully developed in 1952, and intermediate processing and handling of zirconium sponge metal was eliminated.

For several years the approved method of purifying hafnium metal on a commercial scale, described in the preceding sections of this Chapter, has been the iodide process. This process reduces the objectionable impurities in hafnium sponge to acceptable levels. The chief disadvantages to the iodide process are the unrecoverable loss of metal and cost.

In 1956, an intensive program was initiated at the Bureau of Mines, Albany, Oregon, station to develop Kroll processed hafnium sponge of a quality suitable for direct casting into ingot by consumable arc-melting techniques. To date, modifications to the Kroll process have not adequately removed impurities in the hafnium sponge. Because of these impurities, the direct arc-melting of sponge has not consistently produced satisfactory ingot, either on the basis of chemistry or on the soundness of the ingot [26].

The electron beam melting process has been under investigation for the production of high purity hafnium.

⁷ Temescal Metallurgical Corp.

⁸ Wah Chang Corp.

The electron beam melting process was originally developed on a semicommercial scale for the purpose of consolidating titanium sponge directly into ingots without the necessity for the preparation of compressed electrodes. In the course of this development work, experiments on the effect of electron beam melting on other metals showed that the process could be used for purification. A theoretical study [27] indicated that the oxygen content of hafnium should be reduced during the electron beam melting of this metal even though the initial experiments failed to demonstrate this. Closer examination of the theoretical study showed that a high degree of superheat of the molten hafnium would be necessary for the proposed purification. Subsequent experiments on a sample of hafnium obtained from the United States Bureau of Mines, Albany, Oregon, confirmed the fact that hafnium could be purified by this technique.

Description of Equipment and Operation

A number of systems have been described in the literature [28-31] for laboratory-scale electron beam melting. The equipment described here is for production. The interior of a typical two-gun melting furnace is shown schematically in Figure 4.7. The feed material is introduced through the upper gun where it is melted. The molten metal drips into a water-cooled copper mold where the lower gun maintains a molten pool. As the ingot is built up, it is lowered in the mold at the same rate by the ingot puller. Completed ingots, usually 48 inches long, are removed through the ingot removal lock without breaking the vacuum as shown in Figure 4.8. The electron gun can be replaced through the gun lock, as illustrated in Figure 4.9, when this becomes necessary because of fouling by condensed vapors. The interior of the furnace vacuum tank is shown in Figure 4.10.

It is essential that the vacuum system be capable of maintaining an operating pressure of 10^{-4} mm Hg in the chamber if the desired purifying action is to take place. A 225-kw production furnace for producing 3- to 6-inch diameter hafnium ingots requires two 32-inch oil diffusion pumps having a combined capacity of 34,000 liters per second at 10^{-4} mm Hg. Each of these pumps is backed by a special booster pump and appropriately matched fore-pumps.

Another essential is a stable high voltage power supply. The circuitry required is shown schematically in Figure 4.11. If, because of outgassing of the metal, the pressure rises too high, it is impossible to maintain a high voltage between the cathode and the melt, and a low voltage discharge may result. To prevent low voltage arcs, a

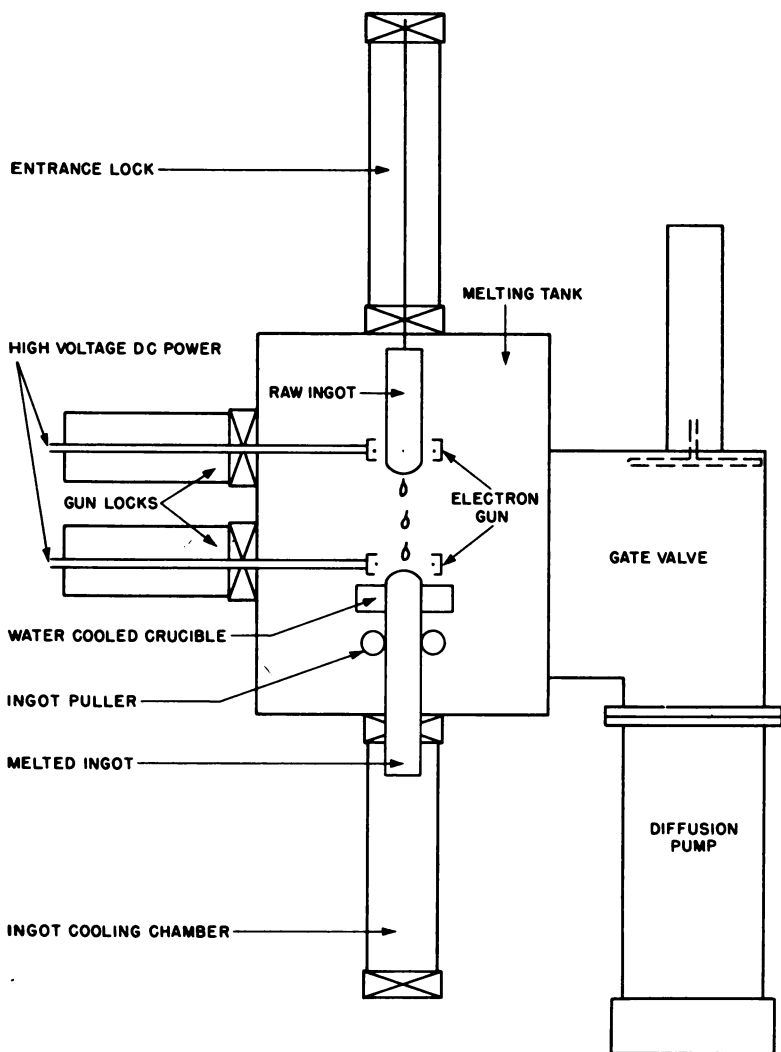


FIGURE 4.7. Schematic of Electron Beam Melting Furnace (C. d'A. Hunt, H. R. Smith, Jr., and C. W. Hanks, *Journal of Metals*, February 1959).

current limiting power input of the type described by Steinmetz [32] places a maximum on the current regardless of the impedance of the cathode-anode gap. The cathode is provided with an emission control circuit, similar to that described by Calverly *et al.* [33], to allow rapid recovery after a voltage breakdown. The voltage usually employed is 4,000–12,000 volts, while the bombardment current from a typical electron gun is variable from 0 to 15 amperes.

A more detailed account of equipment and operation has been reported by the authors [27].

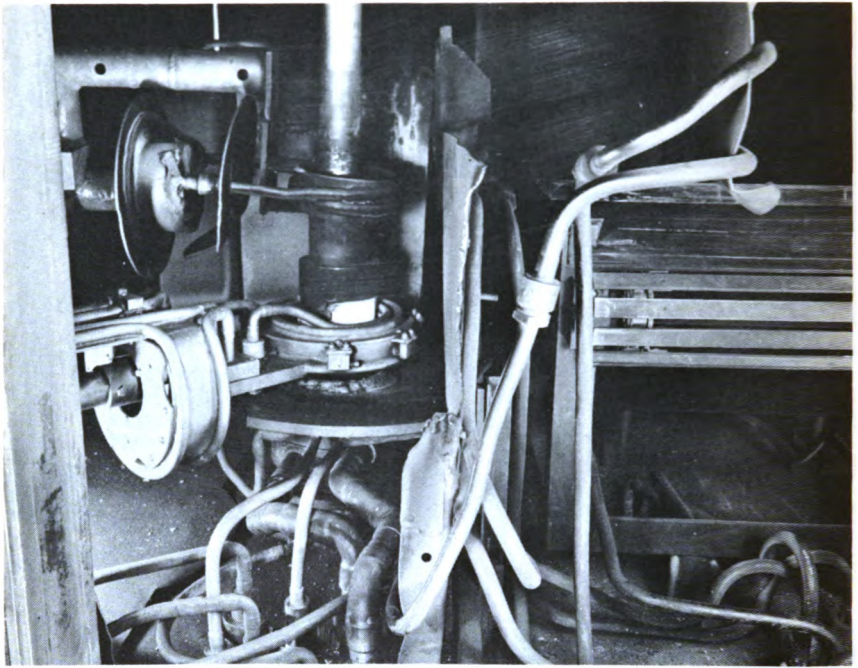


FIGURE 4.10. Interior Mechanism of Electron Beam Furnace (C. d'A. Hunt, H. R. Smith, Jr., and C. W. Hanks, *Journal of Metals*, February 1959).

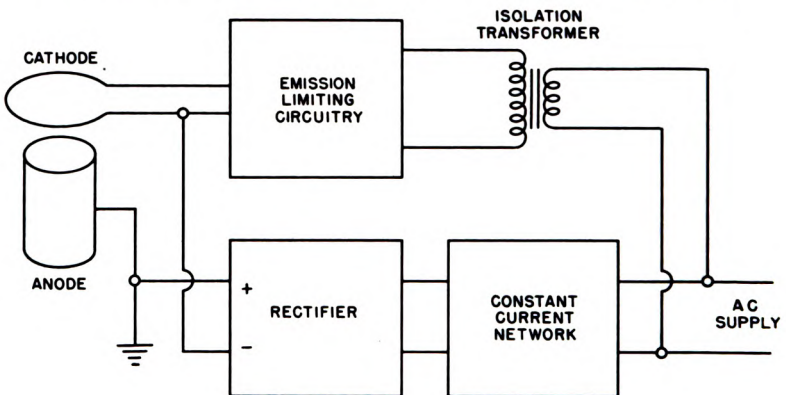


FIGURE 4.11. Electron Bombardment Power Supply (C. d'A. Hunt, H. R. Smith, Jr., and C. W. Hanks, *Journal of Metals*, February 1959).

Composition Changes During Melting

From a metallurgical point of view, the electron beam melting system is interesting in that it not only provides for a high vacuum at the surface of the melt, but also provides (a) for stirring of the melt, (b) for controlling the degree of superheating above the melting point, and (c) for controlling the length of time the metal is molten.

It is thus possible to preferentially volatilize certain constituents from the melt. In the case of constituents forming nearly ideal solutions with the molten base metal, the changes in composition resulting from evaporation of constituents more volatile than the base metal can be estimated from vapor pressure data such as those tabulated by Stull and Sinke [34]. Constituents having a tendency to form intermetallic phases with the base metal are likely to exhibit nonideal solution behavior in the melt, and the approximate vapor pressure over the melt can be derived from a knowledge of the vapor pressure of the constituent over the intermetallic phases. Such data are generally not available for metals such as hafnium, however.

The method for the prediction of the probable composition of a metal after electron beam melting can best be illustrated by an example. Such a case is iron in hafnium, shown on a Cox Chart, Figure 4.12. The vapor pressure of iron at $2,900^{\circ}\text{C}$, corresponding to highly superheated hafnium, is shown to be about 2 atmospheres. Assuming an ideal solution of iron in hafnium at this temperature, the concentration of iron to give a vapor pressure of 2×10^{-5} atmosphere, the

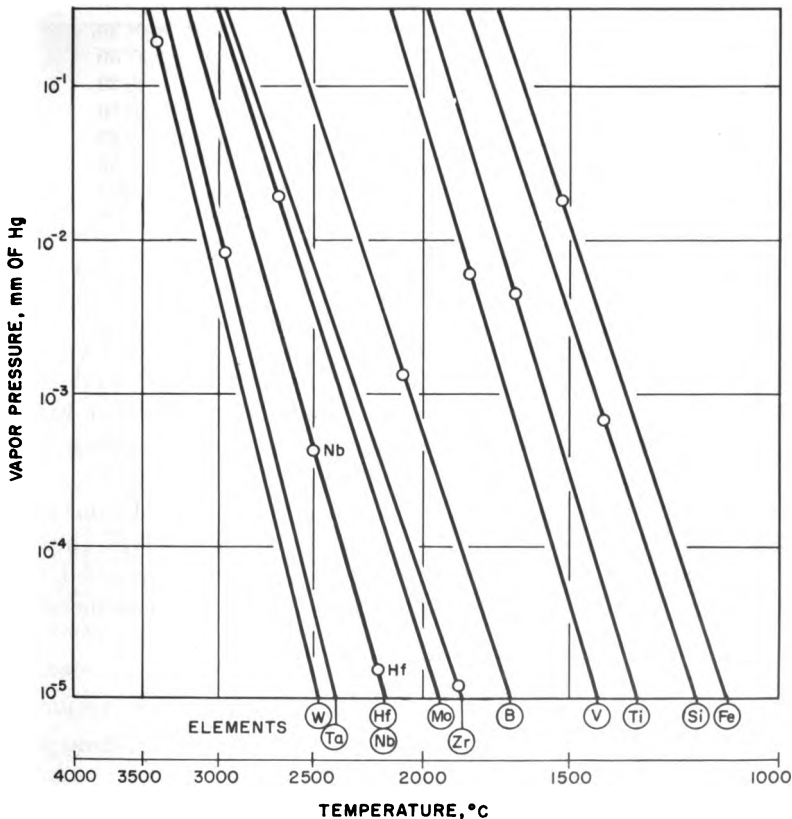


FIGURE 4.12. Vapor Pressure Chart for Metals.

519561 O-60-10

vapor pressure of hafnium at 2,900° C would be about 10^{-5} mol fraction iron or about 3×10^{-6} weight fraction iron in hafnium. The analysis of hafnium shown in Table 4.6 shows that the iron content is reduced below the detection level of 50×10^{-6} weight fraction iron.

A similar calculation on titanium in hafnium indicates a lower limit of 25×10^{-6} weight fraction titanium, compared with the listed analysis of 10×10^{-6} weight fraction titanium, which is in fair agreement with the estimate.

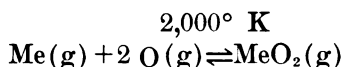
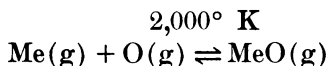
TABLE 4.6—EFFECT OF ELECTRON BEAM MELTING ON THE IMPURITIES IN HAFNIUM METAL

(Analysis in ppm)

| <i>Element</i> | <i>Starting Material</i> | | <i>Electron Beam Ingot</i> | |
|-------------------|--------------------------|---------------|----------------------------|---------------|
| | <i>Top</i> | <i>Bottom</i> | <i>Top</i> | <i>Bottom</i> |
| Al..... | 60 | 75 | 25 | 25 |
| B..... | 7 | 3 | 0.3 | 0.5 |
| C..... | 30 | 30 | 30 | 30 |
| Cd..... | 1 | 2 | 1 | 1 |
| Co..... | 5 | 5 | 5 | 5 |
| Cr..... | 40 | 50 | 20 | 20 |
| Cu..... | 30 | 30 | 30 | 30 |
| Fe..... | 110 | 140 | 50 | 50 |
| Mg..... | 10 | 10 | 20 | 20 |
| Mn..... | 10 | 10 | 10 | 10 |
| Mo..... | 40 | 40 | 40 | 40 |
| N..... | 35 | 63 | 28 | 35 |
| O..... | 850 | 1100 | 298 | 266 |
| Si..... | 200 | 200 | 70 | 70 |
| Ti..... | 100 | 120 | 10 | 10 |
| Zr (percent)..... | 2.2 | 2.1 | 1.8 | 1.4 |
| Average BHN..... | 188 | | 171 | |

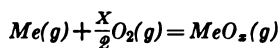
Similar calculations for silicon indicate a lower limit of 50×10^{-6} weight fraction silicon in hafnium, compared with the observed value of 70×10^{-6} weight fraction silicon. The higher observed value is not unexpected in view of the known intermetallic bonding effects between silicon and hafnium.

An interesting and useful fact is that the monoxides of some metals exhibit a higher vapor pressure than the metals themselves, thus providing a means by which deoxidation can be accomplished. The reactions involved in volatilizing suboxides from the base metal are:



The equilibrium constants for these equations can be calculated from Brewer's [35] values for the heats of formation at 2,000° K and from estimated entropy values. The equilibrium vapor pressures of the monoxides and dioxides can then be calculated from the known vapor pressure of the metals and assumed oxygen partial pressure. Because of the lack of data, it is necessary to assume the oxygen partial pressure equal to that of the known titanium-oxygen system. The vapor pressure of metal monoxides at 2,000° K so estimated are presented in Table 4.7. The vapor pressures of the higher oxides were found to be unimportant.

TABLE 4.7—ESTIMATED VAPOR PRESSURE OF METAL MONOXIDES AT 2,000° K



| <i>Metal</i> | <i>Metal vapor pressure (atmosphere)</i> | <i>Monoxide vapor pressure (atmosphere)</i> |
|--------------|--|---|
| Ti----- | 10 ^{-4.9} | 10 ^{-4.4} |
| Zr----- | 10 ^{-8.7} | 10 ^{-6.5} |
| Hf----- | 10 ^{-11.2} | 10 ^{-7.3} |
| B----- | 10 ^{-7.6} | 10 ^{-5.3} |

Deoxidation in Hafnium

The mechanism of metal suboxide volatilization may be applied usefully in estimating deoxidizing tendencies in impure hafnium. Reference to Table 4.7 shows that hafnium suboxide should vaporize from a mixture of hafnium with oxygen. However, the low vapor pressure of hafnium suboxide at the temperature of 2,000° K shows the necessity of a very high degree of superheat to raise the vapor pressure of this species up to the order of 10⁻⁵ to 10⁻⁴ atmospheres.

Of importance in the hafnium system also are the estimated vapor pressures of the boron, titanium, and zirconium monoxides. These species are estimated to be considerably more volatile than hafnium monoxide so that, even in dilute solutions of boron, titanium, and zirconium in molten hafnium, the evaporation of the respective monoxides is undoubtedly possible.

Comparison of the analyses of arc-melted ingot with electron beam melted ingot, Table 4.6, shows a marked reduction in the boron and zirconium content that is unexplainable on the basis of the vaporization of the metallic species boron and zirconium from the melt. The loss of boron monoxide and zirconium monoxide is possible, however, and is most probably the mechanism for the reduction in the concentration of these elements during the electron beam melting purification cycle. The low residual concentration of boron is such that the majority of the oxygen loss then is undoubtedly via the mechanism of either hafnium monoxide or zirconium monoxide evolution.

The total changes in oxygen and zirconium contents correspond very closely to the atomic weight ratio of zirconium and oxygen. Thus, it is possible that the predominant mechanism for reduction in oxygen concentration in hafnium is the loss of zirconium monoxide rather than hafnium monoxide. Further, the fact that the titanium content of electron beam melted hafnium is one-third of the lower limit estimated on the basis of the evaporation of the metallic element itself indicates that some loss of titanium monoxide also occurs. The possibility that the deoxidation of hafnium could be performed at lower degrees of superheat via the evolution of titanium and other metallic monoxides will be explored experimentally in the near future.

Some problems have been encountered in melting by the electron beam process. The large amount of volatiles given off by the hafnium sponge in the first melt gives rise to excessive splattering, making operations difficult. There is also difficulty in connection with lowering the ingot as casting proceeds. The upper part of the ingot tends to bind against the crucible, and the stresses set up in pulling the ingot downward produce tears in the ingot surface. Since only a few ingots have been produced and experience is very limited, solutions to these problems will undoubtedly be worked out. Conventional consumable arc-melting of the first and last melts, for example, would overcome these difficulties, while purification would be achieved in one or more intermediate electron beam melts.

Properties of Electron Beam Melted Hafnium

Electron beam melted hafnium ingots have been fabricated into strip and plate using methods similar to those employed on direct arc-cast and iodide-process ingots [36] and described in Chapter 5. Sheet as thin as 0.015 inch has been successfully cold rolled without cracking, and reductions in excess of 50 percent have been made between anneals.

In Table 4.8, the tensile properties of electron beam hafnium strip are compared with those of strip fabricated in a similar manner using

iodide-process hafnium. Although the heat treatments given the two types of material represented in Table 4.8 are not identical, it is evident that the tensile properties of the electron beam melted material are essentially equivalent to those of arc-melted iodide process material. This is also evident when further comparison is made with the data in Table 7.11 (Chap. 7).

Unfortunately, the corrosion resistance of electron beam melted hafnium in high temperature water and steam has thus far proved to be highly variable. In some cases corrosion resistance is comparable with that of arc-melted crystal bar material; in other cases, it is unsatisfactory. In the unsatisfactory material, corrosion attack is nonuniform and banded in nature. The reason for the poor corrosion resistance of this material has not yet been established.

Summary

It has been shown that impurities can be effectively removed from hafnium by means of the electron beam melting process. The difficulty with the variable corrosion resistance of hafnium melted by this process must be understood and overcome before it can replace conventional processing.

TABLE 4.8—MECHANICAL PROPERTIES OF HAFNIUM STRIP

HOT ROLLED AND ANNEALED

| | <i>Electron Beam</i> | <i>Iodide Process [38]</i> | |
|-------------------------------------|---------------------------|----------------------------|----------------------|
| Anneal..... | 920° C (1,690° F) 1 hr | 900° C (1,650° F) 20 hr | |
| Test Temperature..... | R.T. | R.T. | 600° F |
| Tensile Strength (psi)--- | 66.2×10 ³ | 59.4×10 ³ | 33.7×10 ³ |
| Yield Strength (psi) (0.2% Offset). | 26.4×10 ³ | 22.4×10 ³ | 11.0×10 ³ |
| Elongation (%)----- | 33 | 35 | 54 |
| Reduction in Area (%)-- | 42 | 38 | 56 |

12 PERCENT COLD ROLLED AND ANNEALED

| | <i>Electron Beam [36]</i> | | <i>Iodide Process [26]</i> | |
|-------------------------------------|---------------------------|----------------------|----------------------------|----------------------|
| Anneal..... | 700° C (1,292° F) 3 hr | | 700° C (1,292° F) 1 hr | |
| Test Temperature..... | R.T. | 600° F | R.T. | 500° F |
| Tensile Strength (psi)--- | 78.4×10 ³ | 52.8×10 ³ | 66.5×10 ³ | 40.3×10 ³ |
| Yield Strength (psi) (0.2% Offset). | 55.8×10 ³ | 43.9×10 ³ | 35.3×10 ³ | 34.8×10 ³ |
| Elongation (%)----- | 26 | 23 | 25 | 45 |
| Reduction in Area (%)-- | 43 | 49 | 37 | 61 |

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MELTING, FABRICATION, AND SHAPING

F. R. LORENZ¹, *Editor*

5.1 INTRODUCTION

Hafnium metal has been utilized almost exclusively for control purposes in nuclear power reactors; hence, essentially only that processing development necessary for this rather limited scope of application has been carried out. The quantities of metal that have been processed since the first few pounds were produced in 1950 have been insufficient to require the development of large-scale, commercial, metal-working techniques and have been handled successfully on a small scale.

The incentive and need for doing extensive work in the area of fabrication process development have been limited by the small quantities of hafnium processed and by the sole application to power reactor control rods. Most of these control rod applications involved design and fabrication problems of the same type. The components have been of such size as to obviate the need for large-scale, commercial operations, so that ingot melting and metal working have been handled easily on a small, pilot-plant scale. There is nothing uncommon about the ingot-conversion techniques. All types of heating methods have been used, and nothing unusual has been experienced in forging or rolling, with the exception of limited cold-working characteristics. These methods produce satisfactory products with no real difficulty. Extrusion of shapes, other than rounds, has never been wholly successful, probably only because of extremely limited development work and the scarcity of metal for such experimentation. Wire products have been produced easily by both swaging and drawing techniques.

It has been possible to apply the welding technology of zirconium directly to hafnium with no difficulty, and only slight modifications of conditions and processes are required. Zirconium machining procedures have also been applied successfully to hafnium work with only a few refinements. The preparation of hafnium for the final

¹ Westinghouse Atomic Power Division.

service environment of hot, pressurized water requires pickling in a manner similar to that used for zirconium. Methods of pickling and rates of metal removal are presented in the text.

5.2 MELTING OF HAFNIUM

By J. G. Goodwin ²

The use of hafnium in control rods for pressurized water reactors requires that it be corrosion resistant to high-temperature (500 to 650° F) water. Impurities such as nitrogen and carbon seriously reduce the corrosion resistance of hafnium and therefore must be minimized if the hafnium is to be suitable for reactor use. The effects of various impurities on the hot-water corrosion resistance of hafnium, as well as the corrosion requirements for hafnium, are presented in Chapter 7. The chemical requirements for reactor-grade hafnium are presented in Table 5.1. The refractory and reactive properties of hafnium and the chemical requirements for its use in pressurized water reactor environments require that contamination during all stages of fabrication be kept to a minimum. In melting, this is accomplished by the use of arc furnaces and vacuum or inert atmospheres. Nonconsumable, nonconsumable followed by consumable, and consumable arc-melting have been used successfully to consolidate hafnium crystal bar into ingots for fabrication [1]. Sponge hafnium can be readily arc-melted into ingots; however, the impurity content of the sponge is such that the resultant ingots are not amenable to fabrication. The U.S. Bureau of Mines [2] has undertaken an extensive program to develop techniques for providing hafnium sponge of a purity that permits melting directly into ingots (see Chap. 3).

TABLE 5.1—IMPURITIES IN TYPICAL HAFNIUM STRIP

| Element | (ppm, unless noted) | Element | (ppm, unless noted) |
|-----------------------------|---------------------|-----------------|---------------------|
| Aluminum..... | 50 | Manganese..... | <10 |
| Boron..... | <5 | Molybdenum..... | <10 |
| Cadmium..... | <1 | Nickel..... | <10 |
| Carbon..... | 50 | Nitrogen..... | 20 |
| Chromium..... | <10 | Oxygen..... | 500 |
| Cobalt..... | <10 | Silicon..... | <10 |
| Copper..... | <50 | Tin..... | <10 |
| Hydrogen ¹ | <30 | Titanium..... | <10 |
| Iron..... | 100 | Tungsten..... | 50 |
| Lead..... | <10 | Zirconium..... | 2. 25% |
| Magnesium..... | <10 | | |

¹ In vacuum-melted material, the hydrogen would be 5 to 10 ppm.

² Westinghouse Atomic Power Division.

The primary impurity contributing to hardness is oxygen. The main source of oxygen contamination in Kroll-process hafnium sponge appears to be oxygen-bearing compounds present in the tetrachloride. The use of mixtures of sodium and vacuum-distilled magnesium to reduce hafnium tetrachloride, the use of filtering devices for chemical removal of impurities from the gaseous tetrachloride, and the dissolution of the tetrachloride in fused salts such as sodium chloride-magnesium chloride mixtures have been investigated and have indicated promise. The bimetal reduction technique has produced material containing 300 to 825 ppm oxygen (normal oxygen content is 1,100 to 1,500 ppm). The filtering technique has produced hafnium sponge with oxygen contents ranging from 550 to 1,100 ppm, depending on the filter used. The dissolution of impurities in fused salts has not progressed to a stage where conclusions can be drawn.

The high-purity requirement, both from a corrosion and fabrication standpoint, has prevented the use of induction melting as a technique for forming hafnium ingots for reactor use. Hafnium readily attacks the crucible material during induction melting and becomes contaminated with the reaction products. Melting has been limited to 4- to 5-inch diameter ingots of about 50 pounds because of lack of demand for larger ingots rather than because of any inherent limitation in the process. Several attempts have been made to melt larger ingots on a commercial basis, but the majority of hafnium ingots have been melted in pilot-plant facilities. The techniques for arc-melting hafnium which are described in this section were developed at Bettis Plant.

Nonconsumable Arc-Melting

Satisfactory ingots can be made by the nonconsumable arc-melting process. This method, which involves melting of small pieces of charge material in a water-cooled, copper crucible with a water-cooled, tungsten-tipped electrode, was employed during the earlier phases of the development of hafnium fabrication [3]. While this method has been superseded by the consumable arc-melting process, the fact remains that a shop equipped only with nonconsumable arc-melting furnaces can produce ingots of acceptable quality.

The first step in the melting of iodide hafnium bars by the nonconsumable arc-melting process is the conversion of bars into feed stock of a suitable size. It has been found that cubes approximately $\frac{1}{4}$ inch square are the largest that can be used for production of sound single-melt ingots. Hafnium crystal bars are converted into feed stock by hot-groove rolling the bars at 1,700° F. Heating for hot rolling is done at 1,700° F for 5 to 10 minutes in an electric furnace in which an atmosphere of flowing argon is maintained to minimize oxygen and nitrogen contamination of the hafnium. The

furnace hearth is kept free of foreign matter which could contaminate the bars. With reductions of approximately 20 percent per pass, each bar is reduced 80 to 90 percent in area prior to reheating. After reheating, the bars are reduced about 60 percent in area, using reductions of 15 percent per pass until the final size of $\frac{1}{4}$ inch square is obtained. These bars are sand-blasted and then pickled in a hot aqueous solution (150 to 180° F) of 45 percent nitric, 3 percent hydrofluoric acid. Next, the rods are chopped to $\frac{1}{4}$ -inch lengths, mechanically blended to reduce chemical heterogeneity, and finally degreased.

Nonconsumable arc-melting is done in a tungsten-tipped-electrode arc furnace (Fig. 5.1) such as that which is described in Reference 4. The furnace is similar in construction to that shown in Figure 5.2, with the exception that the consumable electrode is replaced with a tungsten-tipped electrode. Ingots 4 to 5 inches in diameter and up to 50 pounds in weight have been melted, the size being limited primarily by the application. A vibrating hopper in the arc furnace is charged with the weight of feed stock to be melted. The furnace is then sealed off, evacuated to 20 microns pressure with a mechanical pump, purged with helium, evacuated again to 10 microns pressure, and filled with a 5-part-helium, 1-part-argon atmosphere at a pressure of 1 atmosphere. Melting is begun by striking an arc on a small quantity of feed stock which has been placed on the bottom of the water-cooled copper crucible. The arc is initiated by lowering the tungsten-tipped electrode until a magnesium ribbon, previously attached to the electrode, touches the bottom of the crucible. As soon as an arc is established, the vibrating hopper is activated and hafnium is fed into the crucible. After approximately one minute, feeding is stopped and the electrode is lowered nearer to the metal pool. This step is termed "puddling," and its purpose is the melting of particles of feed stock which may have sunk to the bottom of the molten pool. Following this the electrode is withdrawn in order to decrease the depth of the molten pool. This step is termed "freezing." The shallow molten pool insures that any solid charge adhering to the bottom can be melted in the subsequent puddling step. The melting cycle, which consists of feeding for 1 minute, puddling for 3 minutes, and freezing for 2 minutes, is repeated until the entire charge has been melted. The ingot is cooled for about 20 minutes before removal from the crucible. Because of the danger of melting through the crucible at the beginning of the melt, the initial puddling depth is not so great as the succeeding ones; therefore, the particles at the bottom of the ingot are not completely melted. To render this portion of the ingot sound, the ingot is inverted in the crucible and the original bottom is remelted. Conditions for nonconsumable arc-melting are summarized in Table 5.2.

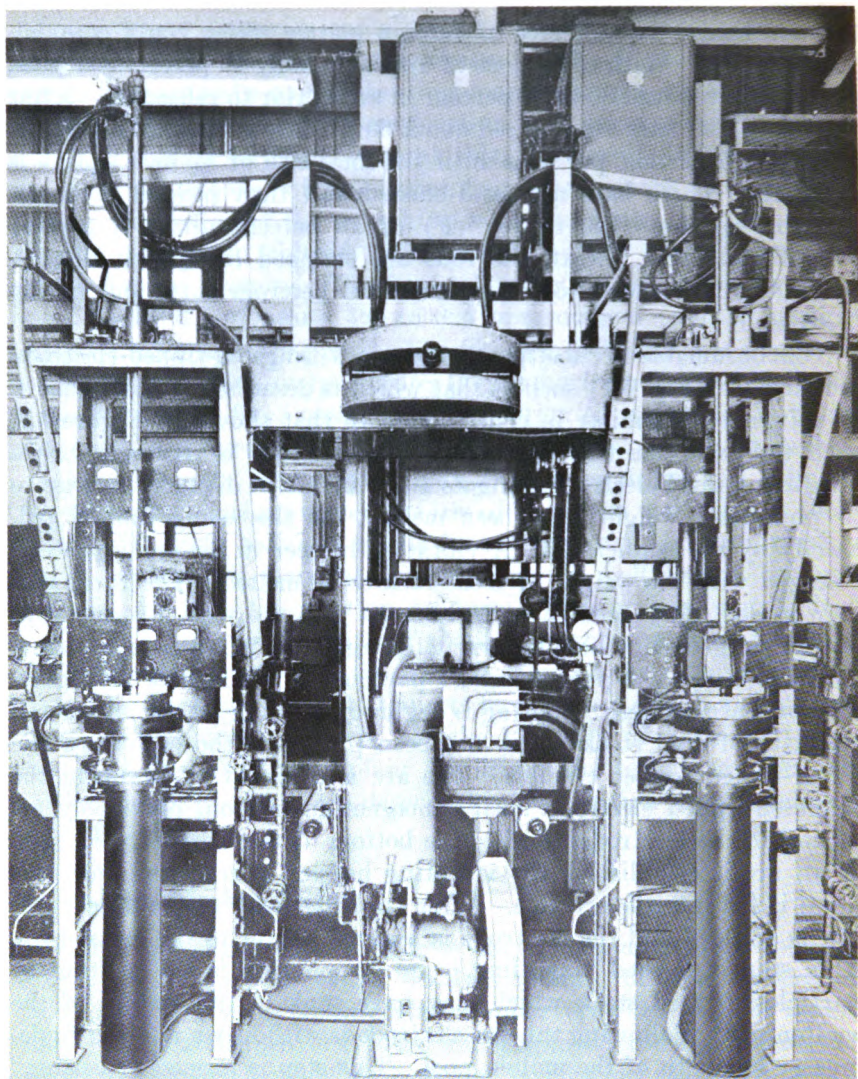


FIGURE 5.1. Tungsten-Tipped Electrode Arc Furnaces for Nonconsumable Arc-Melting (from Ref. 6 Courtesy of American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc.).

TABLE 5.2—CONDITIONS FOR NONCONSUMABLE ARC-MELTING

| | |
|--------------------|--------------------------------------|
| Electrode tip..... | Tungsten. |
| Current..... | 1000 to 1100 amp. |
| Voltage..... | 48 to 50 volts (electrode negative). |
| Atmosphere..... | 1 part argon: 5 parts helium. |
| Pressure..... | 1 atm. |
| Melting rate..... | one-sixth lb/min. |

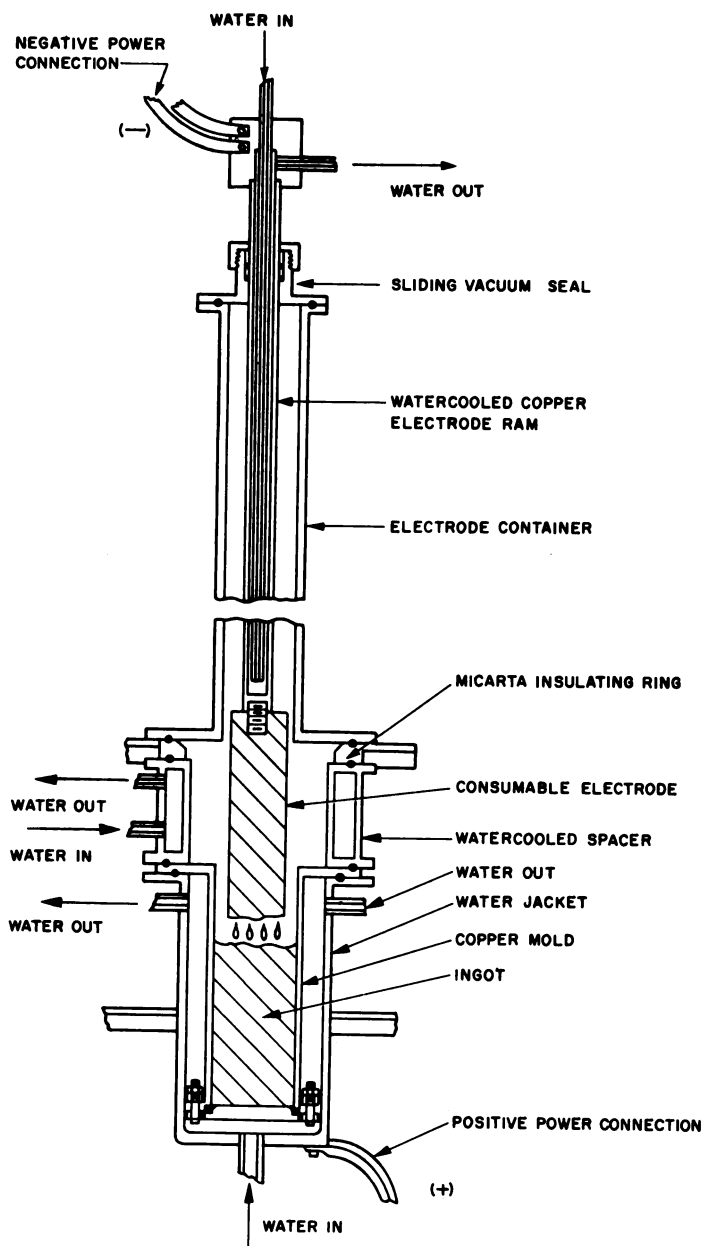


FIGURE 5.2. Diagram of Tungsten-Tipped Electrode Arc Furnace (from W. J. Hurford and F. R. Lorenz, *Journal of Metals*, September 1955, Courtesy of American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc.).

Yields from iodide hafnium crystal bars to conditioned ingots arc-melted by the nonconsumable method have consistently been in the neighborhood of 97 percent. Although the nonconsumable arc-melting technique has an extremely high yield, it has the following inherent disadvantages:

- (a) The hafnium crystal bars must be fabricated into feed stock. This involves considerable expense.
- (b) The hafnium crystal bars are subjected to contamination by oxygen and nitrogen during the hot-groove rolling operation. Laps and seams which may develop in the bars trap oxide that cannot be removed during subsequent blasting and pickling operations.
- (c) Metal is lost as oxide during hot-rolling the crystal bar and in the subsequent pickling operation.
- (d) The melting rate is low, approximately one-sixth lb/min.
- (e) There is a possibility of voids and unmelted pieces in the ingot.

Tungsten and thoriated tungsten (1 to 2 percent ThO_2) serve equally well as electrodes for the nonconsumable melting of hafnium. These materials have the essential characteristics of high melting point, low vapor pressure at operating temperature, sufficiently high thermal conductivity to prevent overheating, sufficient electrical conductivity to carry melting currents, and good mechanical strength at high arc currents. The tips employed vary from $\frac{1}{2}$ to $\frac{3}{4}$ inch in diameter, and $\frac{3}{4}$ to $1\frac{1}{2}$ inches in length and are usually threaded into the water-cooled copper electrode. Graphite is not used as an electrode because the carbon pickup in the ingots would be excessive. Other techniques such as coating a graphite tip with the metal to be melted and making tips composed of metals, carbides, and oxides have not proved successful. Hoge [5] investigated several materials: $\text{Zr} + \text{ZrO}_2$; $\text{Zr} + \text{ZrC}$; $\text{ZrO}_2 + \text{ZrC}$; and $\text{Zr} + \text{ZrO}_2 + \text{ZrC}$. In these cases, the thermal and electrical characteristics were so poor that the tips melted after a few minutes' use.

Double Arc-Melting

The double arc-melting technique [6], nonconsumable followed by consumable arc-melting, eliminates some of the disadvantages of the nonconsumable melting method previously described. Briefly, the method involves consumably remelting a $2\frac{1}{2}$ - to 3-inch diameter, non-consumably melted ingot into a 4- to 5-inch diameter ingot. The first step of this process is to prepare the iodide hafnium crystal bars for nonconsumable melting into a $2\frac{1}{2}$ -inch diameter ingot (see previous section). A reusable threaded stub from a previous consumable melt is placed at the bottom of the $2\frac{1}{2}$ -inch diameter copper crucible. This serves two purposes: one is to provide material on which to start the melt without contaminating it with copper, and the other

is to provide a threaded portion for connection to the copper electrode for the subsequent consumable melt. The desired weight of prepared feed stock is charged into the vibrating hopper of a tungsten-tipped-electrode arc furnace. The furnace is sealed, evacuated to a pressure of 20 microns, purged with helium, evacuated to 10 to 15 microns pressure, and filled to 1 atmosphere pressure with a mixture of 2 parts helium and 1 part argon.³ (See Table 5.3.)

TABLE 5.3—CONDITIONS FOR DOUBLE ARC-MELTING [6]¹ (NON-CONSUMABLE FOLLOWED BY CONSUMABLE)

| | <i>First Melt</i> ² (Nonconsumable) | <i>Second Melt</i> ³ (Consumable) |
|----------------------------|--|--|
| Melting rate..... | 1 lb/min..... | ca. 3 lb/min. |
| Atmosphere..... | 1 part argon: 2 parts helium. | 1 part argon: 1 part helium. |
| Pressure..... | 1 atm..... | 1/6 atm. |
| Current..... | 1,200 to 1,800 amp..... | 2,300 to 2,500 amp. |
| Voltage ⁴ | 38 to 42 volts..... | 30 to 35 volts. |

¹ Courtesy of American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc.

² 2½-in. diameter, 35 lb.

³ 4-in. diameter, 35 lb.

⁴ Electrode negative.

An arc is struck on the ingot stub at the bottom of the crucible, and metal is fed into the molten pool from the vibrating hopper. The iodide hafnium chunks are fed into the molten pool a few at a time. As soon as these are melted, more metal is fed into the melt. The melting rate is about 1 lb/min. It is not the purpose of the non-consumable melt to make a sound ingot, but simply to consolidate the iodide hafnium chunks into a shape which can be consumably melted. Melting is done as rapidly as possible while still producing a coherent ingot. A single-melted, 2½-inch diameter ingot is shown in Figure 5.3.

The stub upon which the nonconsumable melt is made has already been drilled and tapped for its previous use as a consumable electrode. The nonconsumable ingot can then be screwed onto the copper electrode of a consumable electrode arc furnace, such as that shown in Figure 5.2. Clean machining scrap or hafnium fines from the feed-stock preparation are placed on the bottom of a 4-inch diameter copper crucible in order to avoid arcing through the crucible on starting. The furnace is then evacuated to 20 microns pressure, purged with helium, evacuated to 10 to 15 microns pressure, and an inert atmosphere of 1 part argon to 1 part helium is intro-

³ The various helium: argon ratios noted in Tables 5.2 and 5.3 are largely established by trial and error. The addition of argon stabilizes the arc. The earlier practice, nonconsumable arc-melting, employed relatively more helium than the later processes because the argon then available was impure. As higher-grade argon became available, higher percentages of argon were employed.

duced. Following this, the furnace is evacuated to approximately $1/6$ atmosphere. In addition to reducing the amount of entrapped gas, the lower pressure employed here promotes a less stable arc which, in turn, produces a greater stirring action in the melt. The arc is struck by touching the electrode to the fines at the bottom of the crucible. Melting is stopped when the desired weight has been

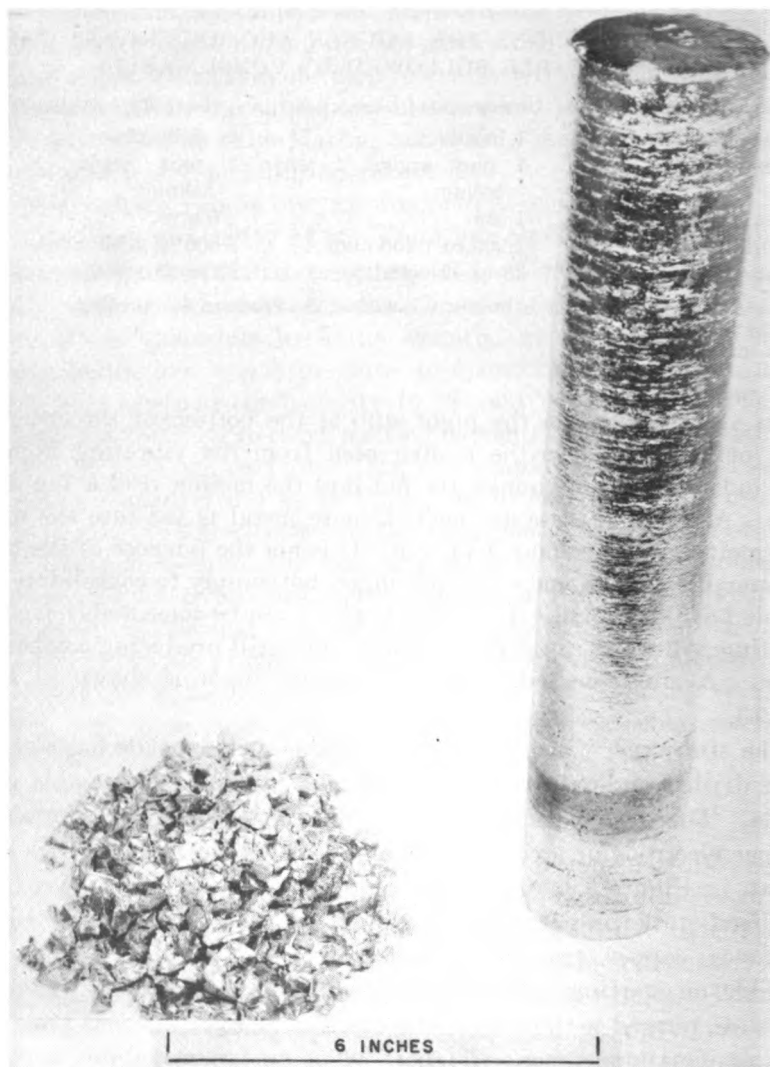


FIGURE 5.3. Chopped Crystal Bar Hafnium Feed Stock and $2\frac{1}{2}$ -In. Diameter Nonconsumable First Melted Iodide Hafnium Ingot (from Ref. 6 Courtesy of American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc.).

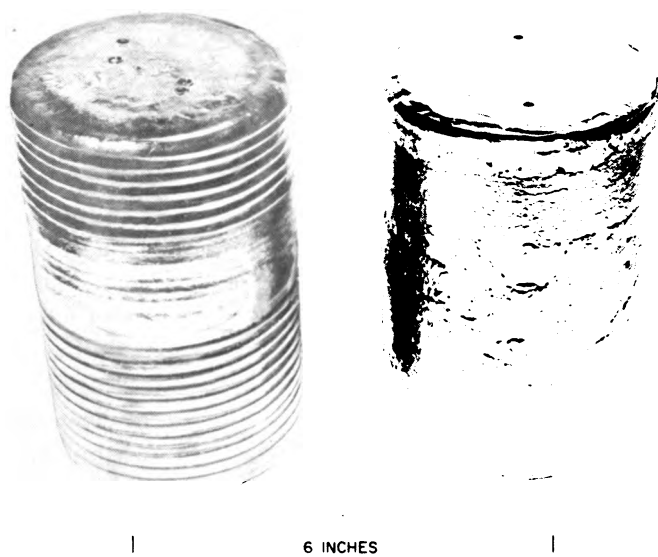


FIGURE 5.4. Left: Weld-Conditioned Consumable Electrode Arc-Melted Hafnium Ingot. Right: As-Cast Consumable Electrode Arc-Melted Hafnium Ingot with Spatter Ring Melted Down (from Ref. 6 Courtesy of American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc.).

melted. The crucible along with the consumable ingot is then transferred to a tungsten-tipped-electrode arc furnace where the spatter ring is melted down and the bottom is remelted. If an exact ingot weight is desired, additions can be made at this time. Figure 5.4 illustrates an as-cast, consumably arc-melted ingot with the spatter ring melted down. Recommended conditions for the double arc-melting process are summarized in Table 5.3.

Consumable Arc-Melting Process

The consumable arc-melting process permits the direct production of sound ingots from iodide hafnium crystal bar and is the preferred melting method. The process is a fairly simple one, employing a consumable electrode made by tack-welding iodide hafnium crystal bars together, as pictured in Figure 5.5. Figure 5.6 shows how the bars are attached to the copper electrode. Because the hafnium crystal bars are not always straight, they are cold-straightened on a forge press prior to assembly into an electrode. After the bars have been tack-welded every 4 inches, using hafnium welding wire, the electrode is vacuum-annealed at 850° C for 1 hour to relieve any residual stress that might cause the electrode to spring apart when melting begins. Melting conditions previously described for consum-

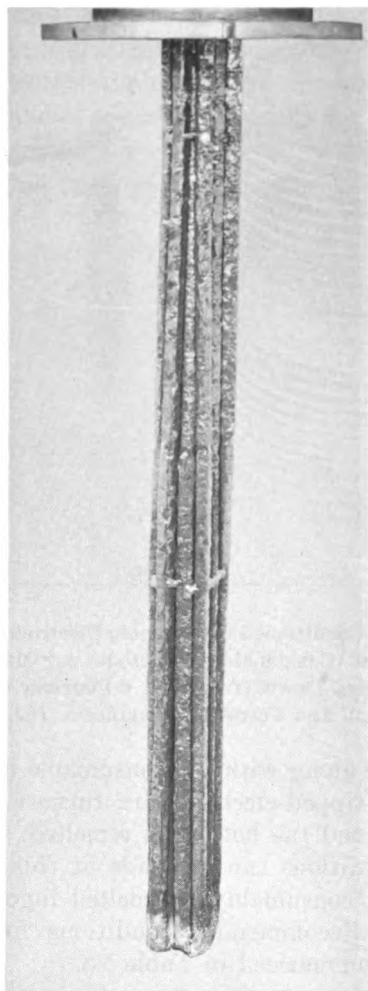


FIGURE 5.5. Iodide Hafnium Crystal Bars Joined for Consumable Arc-Melting (from Ref. 6 Courtesy of American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc.).

able arc-melting are used except for slightly higher currents (2,800 to 2,900 amp). By constructing the electrode so that the crystal bars are joined as shown in Figure 5.7, the ingot weight can be controlled to ± 0.1 pound. The exact amount to be melted is weighed out, and the electrode is constructed. The weight to be melted is that contained in Section A-B in Figure 5.7. Melting is stopped when the large-diameter section is consumed. As in the previously described melting technique, the consumable ingot and its crucible are transferred to a tungsten-tipped-electrode arc furnace where the spatter ring is melted down and the bottom is remelted.

Other Factors in Melting

Scrap Additions

Solid scrap such as end tailings and edge trim can be added in several ways, depending upon the melting technique being utilized. It is necessary to blend the scrap uniformly with virgin material to prevent accumulation of undesirable elements such as oxygen and nitrogen. In the case of nonconsumable arc-melting, scrap can be added by mechanically blending the sized, chopped, and cleaned pieces with the raw material of the charge. Scrap can be added to consumable melts by tack-welding strips of clean scrap to the electrode [7]. Machining scrap is not recycled because of the oxygen and nitrogen contamination which is acquired during machining. It has been the practice to add 30 percent solid scrap to each melt. Although several isolated ingots of 100 percent solid scrap have

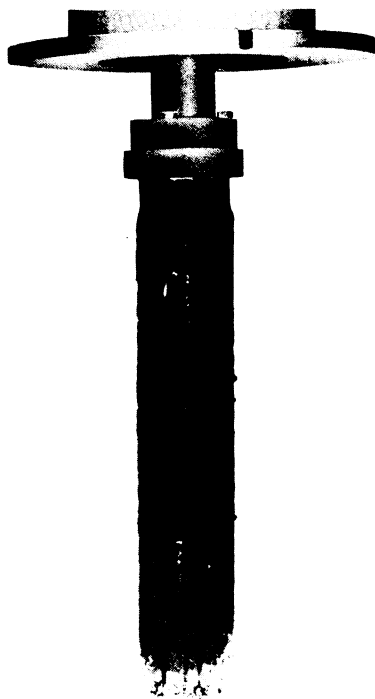


FIGURE 5.6. Tack-Welded Hafnium Crystal Bar Electrode Near Completion of Consumable Arc-Melt Showing Attachment of Crystal Bars to the Copper Electrode (from Ref. 6 Courtesy of American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc.).

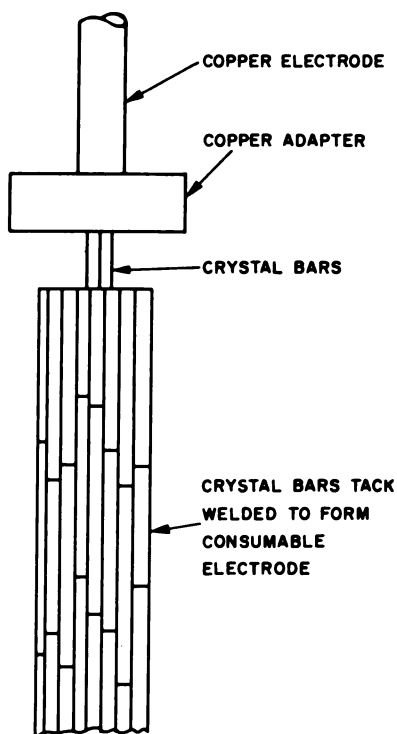


FIGURE 5.7. Diagram Showing How Iodide Hafnium Bars Are Joined into a Consumable Electrode (from Ref. 6 Courtesy of American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc.).

proved satisfactory with respect to fabrication, corrosion, and chemistry, a conservative limit of 30 percent solid-scrap additions to any ingot has been set. This limit not only provides a safety factor for maintaining impurity elements at low levels, but also permits utilization of all the solid scrap generated during control-rod manufacture.

Ingot Conditioning

Until the innovation of surface fusion, iodide hafnium ingots were conditioned by spot-grinding to remove melting ridges or porous areas which might affect the quality of the fabricated shape. Surface fusion is accomplished by rotating an ingot on a lathe fixture (Figure 5.8) and running an autogenous weld bead over the periphery in a chamber under a helium or argon atmosphere at a pressure slightly greater than one atmosphere using a thoriated tungsten welding electrode. Power requirements are 250 to 300 amp at 17 to 24 volts. Material losses in this type of ingot conditioning are negligible. The ingot shown in Figure 5.4 was conditioned by surface fusion.

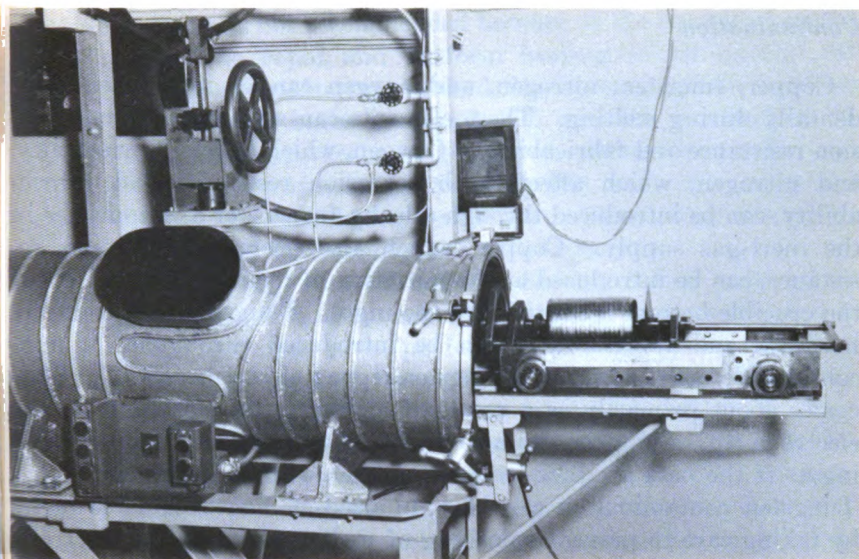


FIGURE 5.8. Lathe Fixture and Chamber Used in Weld-Conditioning of Hafnium Ingots (from Ref. 6 Courtesy of American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc.).

Surface fusion has a distinct advantage over other types of conditioning in that it removes most of the porosity usually found beneath the surface of arc-melted ingots. Prior to the advent of surface fusion, the porosity beneath the surface appeared on hot-rolled plates as surface defects, requiring a machining allowance of about 15 percent more than that for weld-conditioned material. Thus, a considerable saving of material is realized by the use of this method of conditioning because less metal is required per plate and less metal is converted to machine scrap.

Although originally developed for short, small-diameter ingots, the surface-fusion process has been adapted for the conditioning of 12-inch diameter, $\frac{1}{2}$ -ton, zirconium alloy ingots.

Ingot Quality⁴

Ingots produced by consumable arc-melting techniques are quite sound. The average hardness of the ingots (171 BHN/3,000 kg) is less than that for ingots produced by nonconsumable methods (184 BHN/3,000 kg). The double-melting method has the advantage of eliminating any chemical heterogeneity which may exist in the crystal bars or scrap used in making up the charge. The single-melting process provides a method for the rapid production of sound ingots.

⁴ Ref. 5.

Contamination

Copper, tungsten, nitrogen, and oxygen can be introduced accidentally during melting. These elements can adversely affect corrosion resistance and fabricability. Oxygen, which affects fabricability, and nitrogen, which affects both corrosion resistance and fabricability, can be introduced through a leaky furnace or as impurities in the inert-gas supply. Copper, which also decreases corrosion resistance, can be introduced at the initiation of melting if a portion of the crucible bottom is melted into the ingot. Tungsten, which affects hardness and fabricability, can be introduced throughout a non-consumable melt in which a tungsten-tipped electrode is used. This comes about primarily as a result of molten metal splashing on the electrode tip. Tungsten can also be introduced in consumably-melted ingots if the bars are tack-welded together with tungsten electrodes. Tungsten contamination can be minimized in nonconsumable melts by taking care to prevent splashing of molten metal on the electrode tip. Tungsten contamination can be eliminated from consumable melts by tack-welding the electrodes with hafnium wire. Copper contamination can be minimized by initiating the arc at very low power levels and by increasing to full power in increments as the amount of metal in the crucible increases. It can be essentially eliminated by the initiation of melting on a plate of hafnium placed on the crucible bottom. Starter plates $\frac{1}{4}$ inch thick with a $\frac{1}{4}$ -inch thick pin in the center are generally employed. Gaseous contamination can be minimized by utilizing inert gases for the furnace atmosphere and by maintaining a leak-tight furnace system.

5.3 HEATING FOR HOT-WORKING

By J. G. Goodwin ⁵

Hafnium reacts with both nitrogen and oxygen in air at elevated temperatures. This reaction forms a gross surface scale and, under it, a diffusion layer containing nitrogen and oxygen in solid solution. Both gases dissolve readily in hafnium, decreasing room-temperature ductility and increasing hardness. Heating of iodide hafnium for laboratory fabrication is generally accomplished in an electric resistance furnace. A constant flow of argon through the furnace is desirable to minimize oxidation of the material. Commercial gas- and oil-fired furnaces, although not ideal, are satisfactory for heating hafnium, providing the proper precautions are utilized; e.g., removal of scale from the furnace, cleaning of the hearth, and protection from direct impingement of the flames. However, the use of com-

⁵ Westinghouse Atomic Power Division.

mercial furnaces is not recommended because of the danger of hydrogen pickup. The rapid and uniform heating of commercial salt baths provides a satisfactory method for heating iodide hafnium. Usually chloride salt baths are employed, with the composition dependent upon the temperature range desired. In addition to the high rates and uniformity of heating offered by salt baths, the molten salt adheres to the surface, reducing oxidation and providing a lubricant for certain types of fabrication, such as extrusion.

The time and temperature limits for heating iodide hafnium depend on a number of factors such as the heating medium, the size of the piece, the operation to be performed, and the amount of metal which can later be removed from the surface. It is best to heat the hafnium to such a temperature that the fabrication operation can be completed in one operation, thereby reducing gaseous contamination.

As is the case with zirconium, hot working is done in the alpha range. Because the atom percent of oxygen in hafnium crystal bar is some six times that in zirconium crystal bar, and because of the higher alpha-beta transformation temperature of hafnium, the hot working temperatures for hafnium are higher than those for zirconium. Thus, arc-melted crystal bar hafnium is forged at 2,000° F, whereas arc-melted crystal bar zirconium is formed at 1,400° F. Similarly, hot rolling of arc-melted crystal bar hafnium is performed at 1,700° F, while arc-melted crystal bar zirconium is hot rolled at 1,400° F.

5.4 FORGING

By R. W. Redlinger⁶

Forging

This section describes press- and hammer-forging of hafnium. Both forging processes are acceptable, and the choice of method depends upon the equipment available. Much of the information on this phase of hafnium metallurgy resides in unpublished reports. The information presented here is rudimentary, but should serve as a guide to further development in the primary breakdown of hafnium ingots. Attempts to develop techniques for the primary working of hafnium were originally conducted about 1951 [8, 9]. Development has progressed at a modest rate at various installations of the Atomic Energy Commission because the incentive for the development of new and improved techniques has been limited by the rather small quantities of material being processed. The published results of these developments are presented in the following sections.

⁶ Westinghouse Atomic Power Division.

Arc-melted hafnium ingots are conditioned and fabricated in a manner similar to that described for arc-melted zirconium by Gordon and Hurford [10]. Four-inch diameter, arc-melted ingots are the common starting stock for the forging operation, but 5-inch diameter ingots have been forged successfully.

Prior to forging of the ingot, surface imperfections are removed by grinding, sandblasting, and etching. Care must be taken to smooth rough spots that could result in folding during forging.

Forging Methods

The similarity of hafnium and zirconium fabricating techniques is evident in the forging operation. However, higher temperatures are required for hafnium since it does not deform as readily as zirconium. While nitrogen and oxygen dissolve in iodide hafnium and decrease room-temperature ductility and increase hardness [11], these effects do not persist to an important degree at hot-working temperatures.

PRESS-FORGING. The most common type of forging used for hafnium is press-forging. Several techniques have been reported, but the more-widely used method of cogging, or initially squaring, the ingot and then reducing the cross section a maximum of 40 percent is the most direct method of reducing the ingot to a slab. It is believed that the cogging operation consolidates the outside surfaces of the ingot and breaks up the coarse-grained ingot structure. Following this operation, a more drastic reduction can be realized without cracking. Several investigators report satisfactory results with this method [6, 12]. When the ingot quality has been impaired by copper or other contaminants, a less-severe forging technique must be used. Press-forging, sometimes utilizing a spreader, bar to get proper flow of the metal at the ends of the forging, has produced acceptable slabs. The ingot must be examined for signs of cracking after each pass. When cracks are detected, forging must be interrupted until they have been removed by grinding.

The pressure required to work an ingot is dependent upon reduction and temperature. The temperature range is somewhat limited, as described above; therefore, pressure depends primarily upon the amount of reduction. In press-forging, the preliminary square and octagon forming of a 4-inch diameter ingot requires an exerted pressure of approximately 25 tsi. As the reduction increases to 40 to 45 percent of the cross-sectional area, a minimum pressure of 35 tsi is required. Less severe operations such as edging and flattening require 1.5 to 3 tsi. These values are illustrative and are not expected to be valid for all forging conditions. A press-forged slab is illustrated in Figure 5.9.

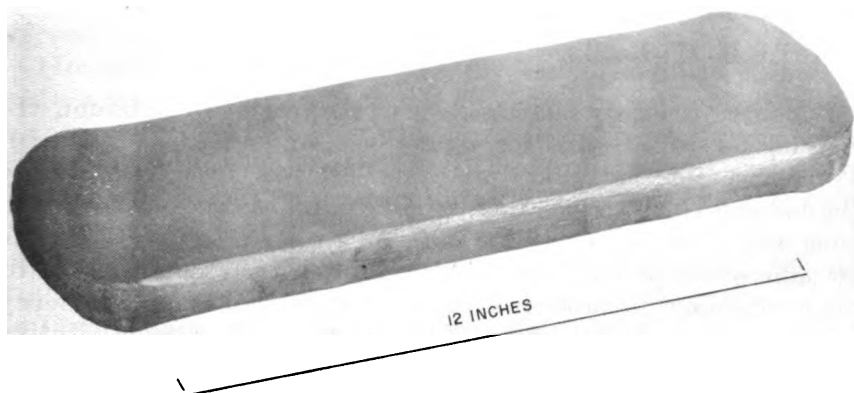


FIGURE 5.9. A Press-Forged Billet for Rolling Made from a 5-In. Diameter Ingot.

HAMMER-FORGING. Forging of 50-pound, 4-inch diameter, arc-melted, iodide hafnium ingots has been successfully accomplished on 2- to 5-ton steam forge hammers [6, 13]. The rapid action of the hammer minimizes heat loss, and therefore, more passes can be made between reheats. Slabs of high quality have been made by using a forging sequence similar to that used in press-forging.

Hafnium forging stock is preheated as described in Section 5.3. The common preheat temperature is 2,000° F, but some forging of hafnium ingots has been done successfully at 1,750 to 1,800° F. To avoid excessive contamination from gases and to reduce oxidation losses, ingots should not be heated above 2,000° F. It has been found that forging should not be continued when the temperature falls below 1,550° F. The general practice is to reheat after every pass to maintain a 1,700° F temperature, but the need for reheating remains a matter of operator judgment.

Quality of Product

The quality of the product depends to a large extent upon the quality of the starting material. The factors affecting the quality of the ingot are discussed at the end of Section 5.2. The removal of imperfections in the surface of the ingot prior to forging is essential, as is the removal of surface defects after each forging step. Hafnium ingots are not appreciably contaminated with metallic impurities during the forging operation. However, it has been reported that the oxygen may be doubled [14].

5.5 ROLLING

By R. W. Redlinger ⁷

Following the early investigations of the forging of hafnium, the demand for rolled strip for reactor use necessitated considerable development of the rolling procedure. It was observed early by Gordon and Hurford [10] that hafnium could be rolled in much the same way as zirconium. Since hafnium readily absorbs gases from the atmosphere at hot-working temperatures, early development of rolling hafnium in protective jackets was performed by Macherey [8]. Concurrently, other investigators were exploring the possibility of heating in an inert atmosphere. The results of these investigations and the information presented by others are reviewed below.

Hot-Rolling

Processes

The arc-melted and forged hafnium ingots described in the foregoing sections are the starting materials for the hot-rolling operation. The surface quality of the final product is dependent upon the condition of the starting material. Prior to hot-rolling, starting stock must be grit-blasted to remove the oxide formed during the forging operation. Surface imperfections detected after grit-blasting must be removed by grinding, blasting, and pickling if the final product is to be free of laps, seams, and slivers.

It has been established that reductions, reheat times, and roll pressures in hot-rolling of zirconium are applicable to the hot-rolling of hafnium. However, a higher temperature is required for hafnium.

Investigation of rolling temperature and other variables has been reported by several workers. Hurford and McClintick, in their work, heated slabs to 1,700° F in an argon atmosphere and hot-rolled in air on a two-high hot mill with 12-inch diameter rolls [14]. Hot-rolling produced an elongated micro-structure similar to that of cold-worked material. A 30-minute anneal at 1,700° F following the last rolling pass yielded a recrystallized structure [12].

Strip made from arc-melted iodide hafnium has been successfully hot-rolled after preheating for 1 hour at 1,700° F. Although lower temperatures have been reported for rolling, 1,700° F appears to be generally accepted. According to one source, rolling should begin at 1,650 to 1,700° F and finish not lower than 1,380° F [11]. From the work undertaken at the U.S. Bureau of Mines, it was found that sponge hafnium could be rolled from 1,740° F to 1,560° F in air [2].

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There is general agreement that hot-rolling temperatures should not exceed the limits presented above.

Hot-rolling of hafnium is generally limited to 15 to 20 percent reductions per pass, each pass being followed by a 15-minute reheal. Larger reductions have been made, but considerable mill error results from the spring-back of the rolls. The capacity of the mill is also a governing factor in reduction limitations, but material properties usually supersede this limitation. The criticality of mill speed is not noticeable in hot-rolling, but the reported values average between 100 and 165 feet per minute.

The metallic contaminants found in hafnium crystal bar are not increased during rolling, but the oxygen and nitrogen content increases several parts per million. The intent is to maintain an oxygen level of less than 900 parts per million.

Product Quality

Hot-rolling may not produce the best quality in certain products, but its ability to produce satisfactory flat products has caused it to become the most extensively used and important method for working hafnium. As in any other metal, the quality of the hafnium product is a function of working techniques, inspection, and conditioning. Working techniques have been fairly standardized as a result of past development, but inspection and conditioning depend largely upon the capabilities of the operator. The importance of slab preparation and inspection cannot be over-emphasized, especially in view of the intrinsic value of the material.

Hot-rolled hafnium strip, fabricated by methods previously described, exhibits a high-quality surface finish after sandblasting and etching.

Product Yields

Yields of hot-rolled products have been shown to be comparable with those of forging, and both are relatively high as compared with other methods of fabrication. With the exception of the tailings cropped from each end of the strip, very little material loss is realized. Strip, 0.250 inch thick x 5.0 inches wide, has been rolled to various lengths depending upon ingot size. A 30-pound ingot yields approximately 55 inches of usable material. Table 5.4 summarizes the fabrication losses and yields in converting crystal-bar hafnium to plate. It is obvious that the rolling operation contributes considerably to the high degree of efficiency obtained. It has been estimated that the rolling yield in producing $\frac{1}{4}$ -inch plate from a 1-inch slab is 96 to 97 percent [12]. Higher total yields could be attained if strip tail loss could be minimized.

TABLE 5.4—FABRICATING LOSSES AND YIELDS IN CONVERTING CRYSTAL-BAR HAFNIUM TO PLATES [14]*Losses*

1. 0.5% loss in groove-rolling crystal bars to $\frac{7}{32}$ -square stock.
2. 1.5% loss in chopping, sifting, and preparing material for arc-melting.
3. 1.8% loss in fabricating 4-in. diameter, 50-lb., arc-cast ingots into plate stock.
4. 11.4% loss in tail material during shearing plates to length.

Yields

1. 97 to 98% yield from corrosion-tested crystal bar to conditioned arc-cast ingots.
2. 85% yield from crystal bar to sheared blanks.

Cold-Rolling

In an effort to conserve hafnium, cold-rolling the product to final thickness instead of hot-rolling, conditioning, and machining to final dimensions has been investigated [16]. Considerable over-all savings were realized by this means.

Processes

The usual starting stock for cold-rolling is previously hot-rolled hafnium which has been sandblasted and pickled to remove the oxide formed during heating. It is usually necessary to remove 0.002 to 0.003 inch per surface by sandblasting and pickling before cold-rolling to insure complete removal of surface contamination.

In cold-rolling, several important variables must be controlled to yield an acceptable product. A number of investigators have reported the effects of reduction, annealing, and impurities and the limitations imposed by them.

Cold-rolling is ordinarily done in conventional, four-high mills although some investigators have used Sendzimir mills and other special equipment. Some work has been done on a four-high mill with 5-inch diameter working rolls. The work reported by Eppelsheimer and Gould [17] was limited to 2-inch rolls.

Cold-rolled hafnium strip has been reduced from cleaned, hot-rolled strip by individual reductions of 7 percent and a total reduction of 30 percent between anneals [6]. Larger reductions have been made, but edge cracking resulted. Total reductions of up to 50 percent can be made, but cracking becomes severe. Edge cracking usually begins at approximately 30 percent reduction, and the cracks propagate rapidly with each succeeding reduction. A curve of hardness as a function of the amount of cold reduction is presented in Chapter 7, Figure 7.16.

The criticality of a 30 percent total reduction between annealing has been noted by several investigators. It was found that cold-rolled hafnium thicker than 0.050 inch may be annealed in air without introducing more than surface contamination provided the times and temperatures are not excessive. When the thickness is less than 0.050 inch, a vacuum or inert atmosphere must be used for annealing. Annealing times and temperatures are determined from the amount of prior cold work and thickness of the section. Figure 7.23 (Chap. 7) presents the effect of various cold-rolling reductions and the temperature range over which recrystallization occurs. It has been suggested that short intermediate anneals at 1,470° F should be adequate for relief of cold-rolling stresses [18].

During an investigation by Eppelsheimer and Gould [17] to determine the texture of cold-rolled hafnium, it was noticed that the zirconium content affected the reductions obtainable. Two samples of arc-melted crystal bar were prepared by the U.S. Bureau of Mines Station at Albany, Oreg. One sample contained approximately 3 percent zirconium as the principal impurity; the other contained 0.01 percent zirconium. The other impurities were reported to be of the order of 500 ppm or less. The reduction possible on the sample containing 3 percent zirconium seemed to be limited only by the rolling equipment available, but the 0.01 percent zirconium strip cracked badly at 60 to 70 percent total reduction. It appears that zirconium in solid solution in hafnium does not impair the cold-rolling properties of the latter, but the presence of dissolved gases may possibly have affected the result. Apparently, oxygen has a greater hardening effect on hafnium metal than on zirconium, since the oxygen impurity levels are comparable in the two metals [2].

Foils have been made at Bettis Plant both by ordinary cold-rolling and by cold pack-rolling. In the latter case, the pack was contained in a steel jacket and has been unsuccessful for foil thicknesses less than 0.007 inch. The quality of the foil is poor because the jacket appears to elongate more than the hafnium so that the foil is torn. It has been possible to cold-roll hafnium foil 0.002 inch thick by 1.5 inch wide experimentally using vacuum-melted material (1.5 w/o Zr, 90-120 ppm O₂, 6-8 ppm H₂, 9-10 ppm N₂). In this case, the material was first hot-rolled to a thickness of 0.050 inch, vacuum-annealed at 1,550° F for 3 minutes, and sandblasted and pickled. After the edges were sheared to remove edge imperfections, the material was cold-rolled to 0.036 inch using 0.003-inch reductions per pass and then annealed at 1,550° F for 30 minutes. Cold-rolling was continued on a two-high jewelers' mill (3-inch diameter rolls) to 0.015-inch thickness using 0.002-inch reduction per pass with manual back tension. Further cold-rolling

was accomplished on the same mill with the rolls set as tight as possible, with 120 passes being required to achieve the final thickness of 0.002 inch. The material was given a final vacuum-anneal at 1,550° F for 30 minutes. This experimental rolling suggests that foils could be readily fabricated on a larger scale using special equipment such as a Sendzimir mill.

Product Quality

The quality of cold-rolled hafnium strip is comparable with that of hot-rolled strip when individual reductions in thickness have not exceeded 7 percent and intermediate annealing follows each 30 percent total reduction. From a corrosion standpoint, cold-rolled hafnium which has been pickled exhibits the same corrosion properties as hot-rolled hafnium [19]. A comparison of the mechanical properties of hot- and cold-rolled strip does not reveal any significant difference after annealing.

The surface finish obtained on strip by cold-rolling is suitable for use in control-rod applications without excessive conditioning. Surface roughness measurements taken on cold-rolled strip have shown its finish to be 60 to 100 μ in. rms or finer, but this factor is limited by the condition of the rolls. A finish of this degree is suitable for most applications.

Yields

Since process losses from cold-rolling are very small, the yields for this process can be expected to be higher than those for hot-rolling where considerable loss is attributed to the oxide film and tail croppings. Analytical data for yields on cold-rolling are not available, but it is estimated that 98 to 99 percent efficiency is obtained for this process.

5.6 EXTRUSION

By R. W. Tombaugh⁸

General

Hafnium is one of the more difficult metals to extrude, a characteristic caused not by an unusually high resistance to deformation, but rather by its galling tendencies when in contact with the extrusion tool surfaces.

Although data are not available permitting the resistance to deformation to be quantitatively separated from the frictional resistance, the short die life experienced in the extrusion of hafnium com-

⁸ Westinghouse Atomic Power Division.

pared with that found for other metals which are difficult to extrude (uranium, uranium-molybdenum, uranium-niobium, zirconium alloys, and various steels) is indicative of this unusually high friction characteristic. The extrusion constant "K" of arc-melted crystal-bar hafnium has been determined experimentally by use of the following formula:

$$P = A_0 K \ln \frac{A_0}{A_1}$$

where

P = total force exerted by the extrusion press (lb)

A_0 = initial cross-sectional area of container (in.²)

A_1 = final cross-sectional area of extruded shape (in.²)

K = extrusion constant (psi)

It will be recognized that the foregoing formula is a simplified form in which the constant "K" includes all frictional resistance to the container and die in addition to the true resistance to deformation.

Control rods, because they often are required to fit into a square or hexagonal reactor-core module, and because a large area must be presented to the neutron flux, usually assume a three- or four-bladed configuration. It would appear that such shapes could be extruded in a single, simple operation; however, results of efforts to date have been discouraging.

Bare-Extrusion Experiments

Both arc-melted sponge hafnium and arc-melted crystal-bar hafnium have been extruded bare by Halapatz [15, 20] into a cruciform shape. The billets for these extrusions were heated in 85 percent BaCl_2 + 15 percent NaCl salt bath at 2,000° F (see Sec. 5.3) and extruded with a 500-ton horizontal press in a 2.600-inch container through a 45° approach die. The dies were made of hot-work die steel with no special facing. The cruciform shape shown in Figure 5.10 had an extrusion (area reduction) ratio of 8.33 to 1. Powdered lead in oil was used as a lubricant in addition to the molten salt adhering to the billet. The arc-melted sponge hafnium extruded

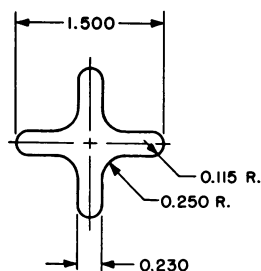


FIGURE 5.10. Cruciform Shape Used in Extrusion Experiments.

through the die but distorted and crumbled. The appearance was believed to indicate hot shortness, and it was suspected that the presence of iron (0.3 percent) in the ingot may have resulted in the formation of a low melting phase. This single sponge billet damaged the die beyond use. Extrusion of the arc-melted crystal bar hafnium was complete and free of tears and cracks, although the surface was rough (Fig. 5.11) and there was some die scoring.

A pressure-temperature relation [21] for the extrusion of bare, arc-melted, crystal-bar hafnium billets indicated the preferred extrusion temperatures. This experiment differed from the earlier work [20] in that it employed $\frac{3}{4}$ -inch diameter, round dies; short, mild-steel billets preceding the hafnium; and MoS_2 added to the lead

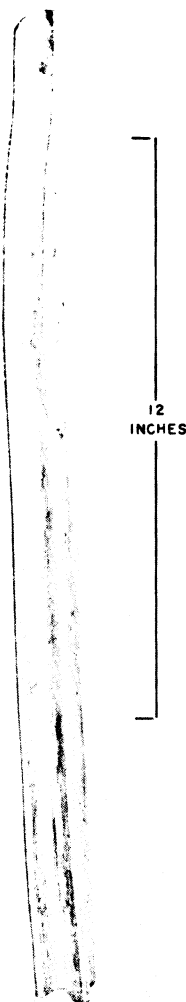


FIGURE 5.11. Arc-Cast Crystal Bar Hafnium Extrusion.

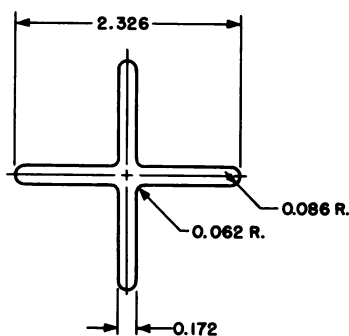


FIGURE 5.12. Cruciform Shape Used in Extrusion Experiments.

lubricant. Additional experiments were performed by Tombaugh [22] using a more difficult cruciform die (Fig. 5.12) with an extrusion ratio of 16.8 to 1, using the $\text{MoS}_2 + \text{Pb}$ lubricant with salt-bath heating. A 1,250-ton horizontal press with a 4-inch diameter container was used; however, because of limited loading, the unit pressure available was less than that used in the preceding experiments. The first two billets heated to 1,900 and 1,950° F, using a cone-face die, stalled in the press. A third billet, using a flat-face die, was tried at 2,200° F and also failed to extrude. A fourth billet was preceded by a copper-nickel starting billet. Both the starting billet and the hafnium billet were heated to 2,200° F, then extruded in tandem through a cone-face die. This arrangement resulted in 25 percent of the hafnium billet extruding with no cracking or tearing, although striations were present. The press stalled before the billet could be completely extruded.

Performance Analysis

The temperature-versus-extrusion constant curve shown in Figure 5.13 is the result of extruding seven billets. The numbering of the points indicates order in which the billets were extruded through $\frac{3}{4}$ -inch diameter, round dies [21]. The chart suggests a diminishing advantage in increasing the temperature above 2,000° F. This is probably due to a breakdown of lubricants since there are no phase changes in this range. The early [20] cruciform extrusion (Fig. 5.10) yielded a "K" constant of 74,500 psi at 2,000° F, which deviates considerably from Figure 5.13. This is hardly surprising in view of differences in shape, lubricant, and starting material involved. In comparing the author's work [22] with the round rod experiment [21], conditions were comparable except for the shape (Fig. 5.12). The "K" constant of the extrusion at 2,200° F was 54,800 psi which, if extrapolated on Figure 5.13, is quite in agreement. This indicates that the penalty for extruding intricate shapes

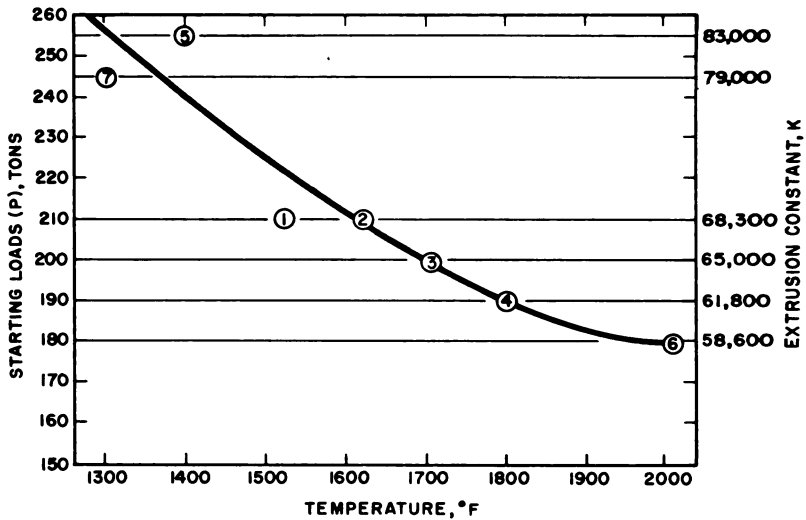


FIGURE 5.13. The Relation of Extrusion Constant to Temperature.

cannot be great, but more importance is attached to the type of lubricant used and the employment of a starting billet of another material. The material of the starting billet must have a somewhat lower "K" constant than the objective material in order to reduce the starting peak pressure of the objective material.

Although the experience mentioned has shown no great differences in pressure requirements for simple and intricate shapes, there are other serious problems such as tearing or cracking, striations, distortion, and short tool life, which are largely dependent on the shape. Often, because of limitations in an available extrusion press, or because of scarcity of material, scaled-down shape models are employed. Such a practice, however, can be misleading. A well-known criterion for measuring the extrusion penalties of various shapes is the "factor" system. The factor is derived by dividing the perimeter of the shapes in inches by the cross-sectional area in square inches. Thus, a shape such as a cruciform in two different sizes can have the same thickness-to-span ratio, yet have different factors. The smaller the proportioned shape, the higher the factor, and consequently, it is considered to be more difficult to extrude. Thus, poor results on a scaled-down shape cannot be conclusive in understanding the extrusion of a full-sized shape.

The "K" constant for the extrusion of the bare hafnium sponge in the single case mentioned was 88,700 psi which is impractically high. The galling of unconsolidated or unmelted sponge is even higher than that of the arc-melted bar, and the abrasive effects upon the die and container present an acute tooling problem. In using an extrusion press for experimentally compacting hafnium sponge

it was found that, during the compacting against a blank die and during the removal of the compact, the abrasion in the container was severe enough to force discontinuance of the practice [23].

Recommended Conditions

Hafnium, having an unusually high "K" constant, should be extruded under maximum unit pressure conditions within the container. This is accomplished by selecting a container size such that the stem is fully loaded. Stem material, length, hardness, frequency of loading, and safety rules place this maximum at 150,000 to 200,000 psi.

Die materials should probably be restricted to high-speed steels or sintered products. Chromium-plated tool surfaces should be avoided because there are indications that hafnium, like zirconium, alloys with chromium during hot extrusion, thereby "loading up" the die and causing striations on the product.

Effective lubrication is a field needing further exploration. Another possible field of investigation is to seek satisfactory materials with which to jacket hafnium during extrusion. A satisfactory jacket could greatly lower the required pressure since, as has been pointed out, a great share of the extrusion "K" constant is attributable to friction.

*Rod and Wire Fabrication*⁹

The similarity between iodide zirconium and iodide hafnium becomes quite evident in the fabrication of rod and wire. Rods have been hot-rolled commercially for use as wire-drawing stock. These have been made by forging a 4-inch diameter ingot to a 1½-inch square with rounded corners, followed by hot-groove rolling at 1,800° F to 5/16-inch round. Each pass in groove-rolling is an oval except the final one. The 5/16-inch diameter rod is then sandblasted and pickled in preparation for a copper electro-deposit. After the rods are copper plated, they are given three baked-lime coatings. The copper and lime serve as lubricants in wire-drawing. Drawing is accomplished by taking individual drafts of 10 to 20 percent and annealing at 1,400° F for 10 minutes after each 35 percent total reduction. Various phosphate coatings developed for drawing zirconium and zirconium-alloy wire have also been found to be suitable for drawing iodide hafnium wire.

Hot-rolled rods can be cold-drawn or swaged by the same procedure as is used for wire-drawing; namely, 10 to 20 percent individual reductions with intermediate anneals at 1,400° F for 10 minutes after each 35 percent total reduction. The lubricants for cold-

⁹ Ref. 6.

drawing are similar to those used for wire-drawing. Swaging does not require lubrication.

5.7 JOINING OF HAFNIUM

By E. H. Sayell¹⁰

Introduction

The utilization of hafnium as a control material for nuclear reactors usually requires that special shapes be fabricated, a typical example of which is shown schematically in Figure 5.14. Welding is the only successful method of fabrication developed for these shapes. Because of the scarcity of hafnium, only that part of the control rod which actually serves a neutron-absorbing function is made of hafnium. An upper extension, identified as an "adaptor plate" in Figure 5.14, is made of Zircaloy-2. This, for mechanical

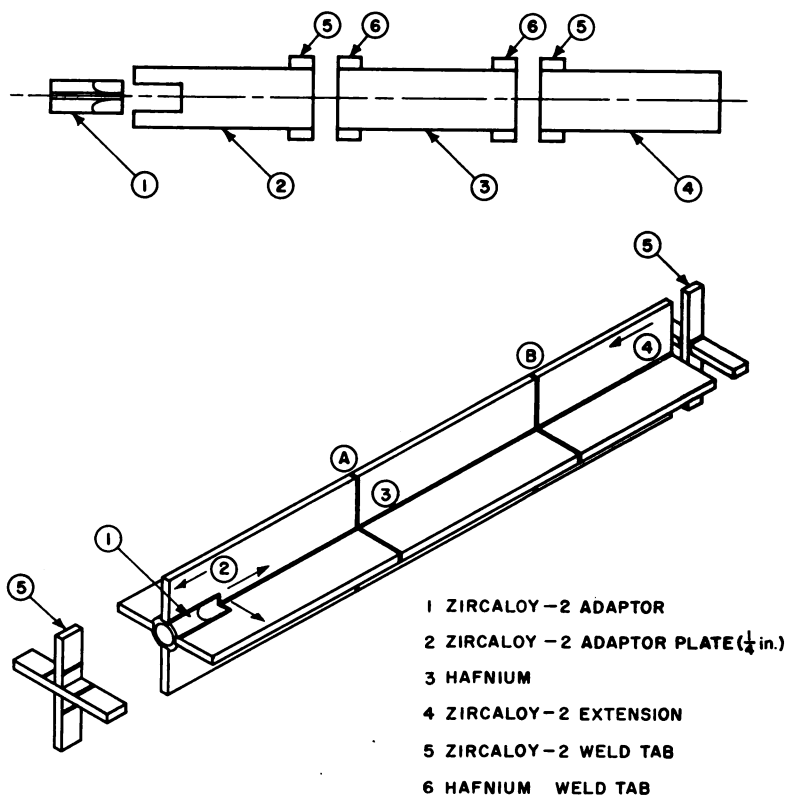


FIGURE 5.14. Schematic Representation of a Typical Control Rod Showing Location of Hafnium Section and Zircaloy-2 Section and Welds; Weld Tab Locations Are Indicated in the Upper Sketch.

¹⁰ Westinghouse Atomic Power Division.

and hydraulic purposes, retains the cruciform shape and serves to connect the control rod to cylindrical rods which are in turn connected to the control-rod actuating mechanisms. At the bottom end of the hafnium section there is sometimes attached a Zircaloy-2 extension for the purpose of minimizing flux peaking which occurs when the control rod is raised during reactor operation. Thus, both hafnium-to-hafnium, and hafnium-to-Zircaloy-2 welds are required to fabricate a typical control rod.

The welds required are shown by the heavy lines in Figure 5.14. Since the total length of the rod may be as great as $10\frac{1}{2}$ feet, and the maximum permissible deviation from straightness is $\frac{1}{32}$ inch, it is clear that distortion in welding must be well controlled. In addition, sound, uncontaminated welds must be made in order to meet the strength and corrosion resistance requirements imposed by the conditions of service.

The welding procedures described here were largely developed at Bettis Plant. While the procedures were determined for a limited range of shapes and sizes, it appears that they can be adapted to other situations with ease.

Tack Welding

Preparatory to fusion welding, tack welding is employed to position the components accurately. Exercise of proper precautions during tack welding saves subsequent tedious straightening. Special fixtures are utilized to align the components for butt and shape welding.

Tack welding is usually done in air to minimize assembly-fixture design problems. The tack welds are generally spaced 3 to 4 inches apart and are approximately $\frac{1}{2}$ inch long. The welding parameters in common use for hafnium and Zircaloy about $\frac{1}{4}$ inch thick are 125 to 135 amps at 14 to 18 volts.

Tack welds made in air are brittle even though a 20 to 25 cubic feet per minute argon flow is maintained over the weld area. During subsequent fusion or seam welding, the contaminants from the air welding are sufficiently diluted that no hard or corrodible spots remain. During fusion welding, the tacked areas cause the arc to wander and the molten pool to flow unevenly; consequently, the number of tacks should be kept to a minimum.

Fusion Welding

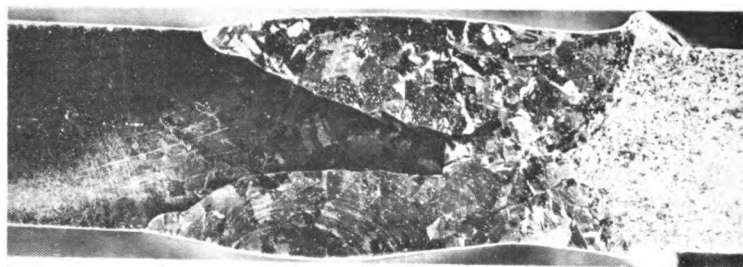
Because of its reactivity with the elements of the atmosphere, hafnium must be isolated during welding operations to insure ductile, corrosion-resistant welds. This is accomplished by means of inert-atmosphere welding chambers which are equipped with suitable fixtures [26].

Before the welding chamber is closed and evacuated, the work should be accurately positioned under the electrode, and the controls and mechanisms should be activated to insure proper functioning and alignment of the work. The use of hand welds should be avoided on long joints because of the limited work area available to the operator and the fact that temperature and pressure build-up within the welding chamber make hand operations difficult. The welding chamber should be evacuated to about 10^{-4} mm Hg, then back-filled with helium or argon to about one atmosphere pressure. The pump-down time required for evacuation is dependent upon the leak rate of the chamber, pumping equipment capacity, and cleanliness of the fixtures and parts. Supplementary details of welding chambers may be found in Reference 4.

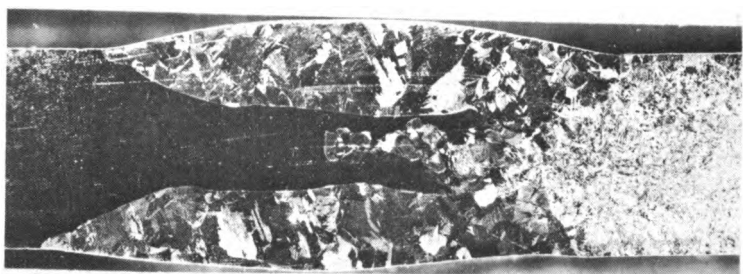
A thoriated tungsten electrode is positioned over welding tabs tacked to the components to prevent melting over the edge of the parts being welded. Each welding pass is started and finished on a welding tab. Welding conditions for butt welds in $\frac{1}{4}$ -inch thick hafnium, hafnium plate, or hafnium-Zircaloy plate are approximately 220 amp at 16 volts with an arc travel of $6\frac{3}{4}$ inches per minute. Both sides of a butt joint must be fused to insure complete penetration.

Since hafnium has a higher melting point than Zircaloy-2, a butt-welded joint between these two materials is made by positioning the electrode on the hafnium side $\frac{1}{32}$ to $\frac{1}{16}$ inch away from the Zircaloy-hafnium interface. It is evident that a pass made directly over the joint would melt more Zircaloy into the weld alloy since the Zircaloy melts at a temperature approximately $1,000^{\circ}$ F lower than hafnium. To counteract this melting point differential, the electrode is positioned on the hafnium side of the joint, and a thin Zircaloy strip is tacked parallel to the seam, on the Zircaloy side, to serve as filler material and to prevent undercutting the Zircaloy plate. The optimum electrode distance concentrates the heat on the hafnium, reduces the possibility of Zircaloy burnthrough, and produces 100 percent penetration.

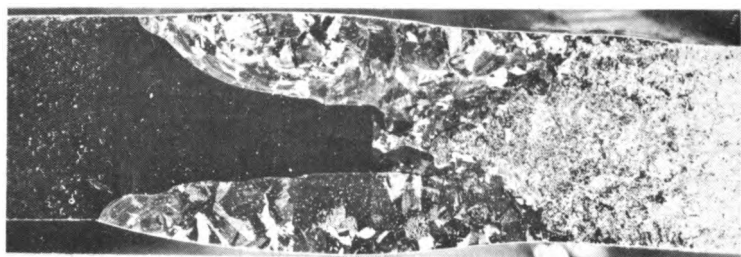
Weld penetration is measured by affixing hafnium and Zircaloy weld runout tabs of the same thickness as the pieces being joined to both ends of the butt joint. After welding, these tabs are removed, polished, etched or heat tinted, and examined at $4\times$ minimum magnification. This method has been substituted for radiographic inspection since film density variations, caused by material density differential and varying degrees of alloying between these metals, result in misleading evaluations of the welds. A standard for hafnium-Zircaloy butt-weld penetration has been used which considers a butt-welded joint 100 percent penetrated if the hafnium has been completely washed with molten Zircaloy-2 for the entire length of



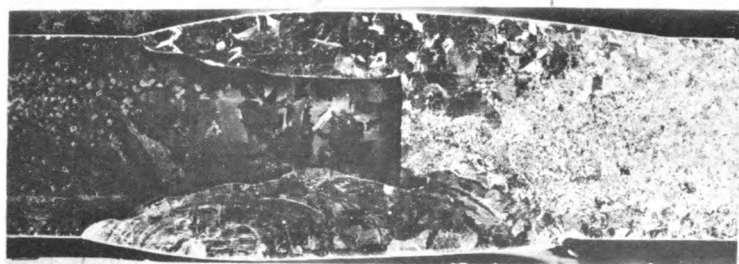
(A)



(B)



(C)



(D)

FIGURE 5.15. Butt Weld Standards for 100 Percent Penetration (Hafnium Is at Left): (a) and (b) Are Acceptable; (c) and (d) Are Unacceptable; 5X.

the weld. This standard, therefore, allows a portion of the hafnium to remain unmelted provided it has been completely contacted by molten Zircaloy-2 throughout the joint interface. The limits of acceptability of the butt-welded joints are shown in Figure 5.15. Figure 5.15 (A) and (B) show the hafnium interface (dark material on left side of macrographs) to be completely surrounded by weld alloy. Figure 5.15 (C) and (D) display welds in which the Zircaloy material failed to become molten across the entire thickness of the joint and, thus, fail to meet the 100 percent penetration requirement for acceptable butt welds.

The thickness of unmelted hafnium was measured at the hafnium-Zircaloy weld interface of tensile test specimens meeting the 100 percent penetration criterion. This thickness was then recorded as a percentage of the total specimen thickness. The corresponding tensile test data were recorded for various degrees of unmelted hafnium in the welded joint. These data, obtained by Sayell and heretofore unpublished, are presented in Table 5.5.

TABLE 5.5—TENSILE PROPERTIES OF HAFNIUM-ZIRCALOY-2 BUTT WELDS AS A FUNCTION OF THE DEGREE OF UNMELTED HAFNIUM IN THE WELD

| Percent unmelted hafnium at joint interface ¹ | Test temperature (° F.) | 0.2% yield strength (psi) | Ultimate tensile strength (psi) | Elongation in 2 in. (%) | Reduction in area (%) |
|--|-------------------------|---------------------------|---------------------------------|-------------------------|-----------------------|
| 25----- | Room | 33, 700 | 59, 500 | 10 | 25 |
| 50----- | Room | 43, 800 | 60, 900 | 10 | 23 |
| 50----- | Room | 32, 600 | 62, 100 | 10 | 20 |
| 50----- | Room | 31, 300 | 67, 200 | 40 | 21 |
| 90----- | Room | 42, 700 | 62, 100 | 10 | 20 |
| 28----- | 500 | 19, 700 | 36, 800 | 28 | 61 |
| 36----- | 500 | 27, 500 | 38, 500 | (?) | 56 |
| 43----- | 500 | 25, 400 | 35, 300 | (?) | 56 |

¹ Percent of the thickness of unmelted hafnium relative to over-all plate thickness.

² Specimen broke near gauge mark. True elongation unobtainable.

The results indicate that the tensile properties of welds 100 percent penetrated are unaffected by the amount of unmelted hafnium.

Precautions To Be Observed During Welding

The following list summarizes the precautions which must be observed to insure satisfactory welds:

- (a) Clean and degrease the welding chamber, all components, and fixtures.
- (b) Ensure that the leak rates of the welding chamber and vacuum system are minimized.

- (c) Start and stop welds on runout tabs to avoid edge melt-down.
- (d) Use automatic controls and drive mechanisms wherever possible to reduce arc wander and variations of weld penetration.
- (e) Avoid touching the thoriated tungsten electrode to the work since this will cause sufficient contamination to adversely affect corrosion resistance.
- (f) Avoid sustained use of any one electrode since a low-melting eutectic of tungsten and hafnium (or Zircaloy) can form on it, drop into the molten pool, and contaminate the weld.
- (g) Use welding-grade helium which contains about 0.05 volume percent of impurities and argon containing about 0.2 volume percent impurities.

Mechanical Properties of Hafnium-Zircaloy-2 Butt Welds

Impact Properties

The impact (unnotched) properties of Zircaloy-hafnium butt-welded specimens were determined as a function of testing temperature by Hoge [24]. In these specimens, the weld was made with the electrode positioned directly over the butt joint. The results are shown in Table 5.6 together with the impact properties of the component materials.

TABLE 5.6—IMPACT VALUES OF HAFNIUM [2] AND HAFNIUM-ZIRCALOY-2 BUTT WELDS [24]

| Material | Impact values (ft-lb) | | | |
|--|-----------------------|-----------------|--------------------|--------------------|
| | Room temperature | 200° F | 400° F | 500° F |
| Zircaloy-2 AC, 1,800° F | 19 | 26. 5 | 34. 5 | ¹ 52. 5 |
| Zircaloy-2 AC, 1,490° F | 23 | 42 | ¹ 67 | ¹ 62 |
| Zircaloy-2 WQ, 1,800° F | 31. 5 | 36. 5 | ¹ 71. 5 | ¹ 68. 5 |
| Zircaloy-2 CW | 10. 5 | 44 | ¹ 67 | ¹ 63 |
| Crystal-bar zirconium | ¹ 37 | ¹ 35 | ¹ 30 | ¹ 28 |
| Crystal-bar hafnium | ¹ 76. 5 | ¹ 74 | ¹ 67 | ¹ 62 |
| Induction-melted commercial Zircaloy-2 | 23-31. 5 | 41 | ¹ 62 | ¹ 59 |
| <i>Weld Samples</i> | | | | |
| Zircaloy-2-hafnium, AC, 1,800° F | 30 | 31 | 56 | ¹ 57 |
| Zircaloy-2-hafnium, AC, 1,490° F | 30 | 33. 5 | 47 | ¹ 46. 5 |
| Zircaloy-2-hafnium, WQ, 1,800° F | 33 | 47 | 24 | ¹ 59 |
| Zircaloy-2-hafnium, CW | 14. 5 | 34. 5 | 11. 5 | ¹ 65 |

¹ Specimen did not break.

Note: AC=Air cooled from temperature indicated.

WQ=Water quenched from temperature indicated.

CW=Cold worked.

Hoge [24] comments that 400° F was necessary to prevent the Zircaloy-2 structures from failing by fracture. As can be seen from Table 5.6, the room-temperature impact values of welded specimens are usually higher than for the base materials, but a temperature of 500° F is required to avoid fracture in the welded specimens. A welded specimen has approximately the same impact values as Zircaloy-2 at 500° F, and, if properly made, fracture will occur in the Zircaloy.

Tensile Properties

Hoge [25] also performed tensile experiments on hafnium-Zircaloy-2 welds made with the electrode directly over the joint. The tensile data are recorded in Table 5.7 (also see Chap. 7). No heat treatment or stress-relief treatments were given to any of the specimens after welding. Values for unwelded hafnium and Zircaloy-2 specimens are compared with the values obtained on welded specimens in Figures 5.16 and 5.17.

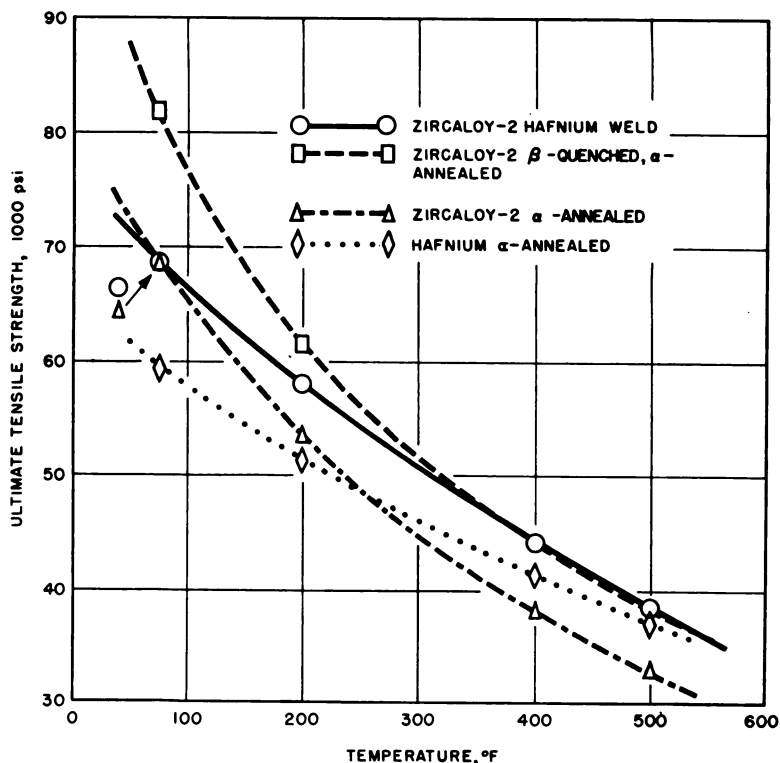


FIGURE 5.16. Ultimate Strength of Hafnium-Zircaloy-2 Welds as a Function of Temperature.

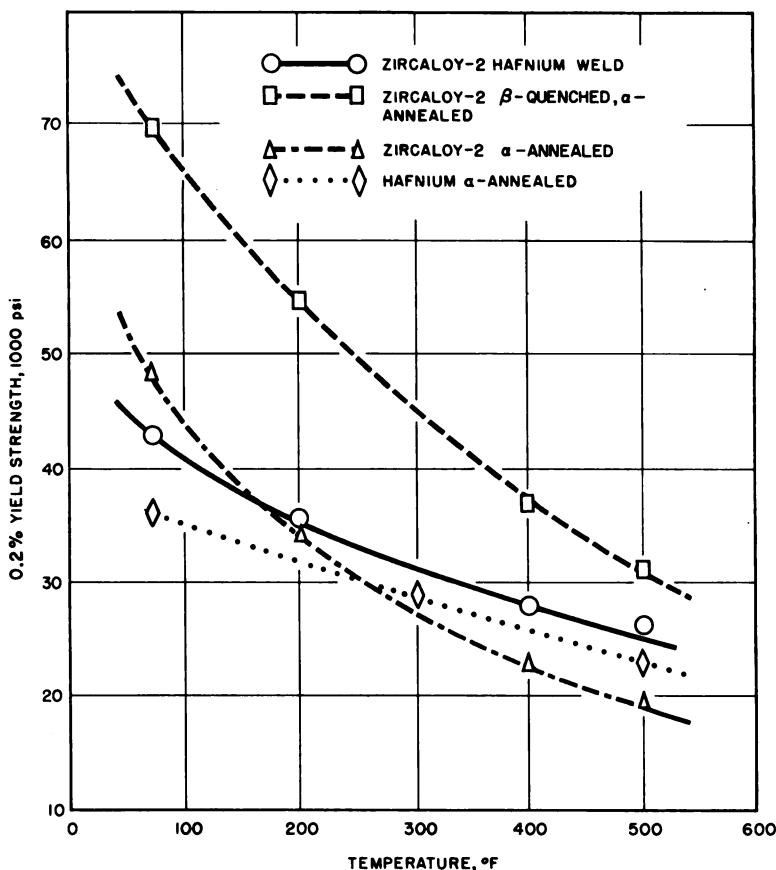


FIGURE 5.17. The 0.2 Percent Yield Strength of Hafnium-Zircaloy-2 Welds as a Function of Temperature.

TABLE 5.7—TENSILE TEST DATA FOR ZIRCALOY-2-HAFNIUM WELD SPECIMENS [25]

| Specimen | Test temperature | 0.2 percent yield strength (psi) | Ultimate tensile strength (psi) | Uniform strain (%) | Elongation in 2 in. (%) | R.A. (%) |
|----------------|------------------|----------------------------------|---------------------------------|--------------------|-------------------------|----------|
| 1 ¹ | Room | | 68,500 | | 9 | 18 |
| 2 | Room | 42,500 | 69,100 | 10.5 | 11 | 12.5 |
| 3 | 200 | 37,300 | 57,500 | 18 | 21 | 26 |
| 4 | 200 | 35,200 | 58,000 | 15 | 16 | 24 |
| 5 | 400 | 27,600 | 44,100 | 18.5 | 26.5 | 44 |
| 6 | 400 | 27,900 | 42,900 | 16.5 | 26.5 | 50 |
| 7 ¹ | 500 | | 38,000 | | 28.5 | 49 |
| 8 | 500 | 25,900 | 37,500 | 14.8 | 26.5 | 48 |

¹ Specimens 1 and 7 were loaded above the yield point before the autographic record was started.

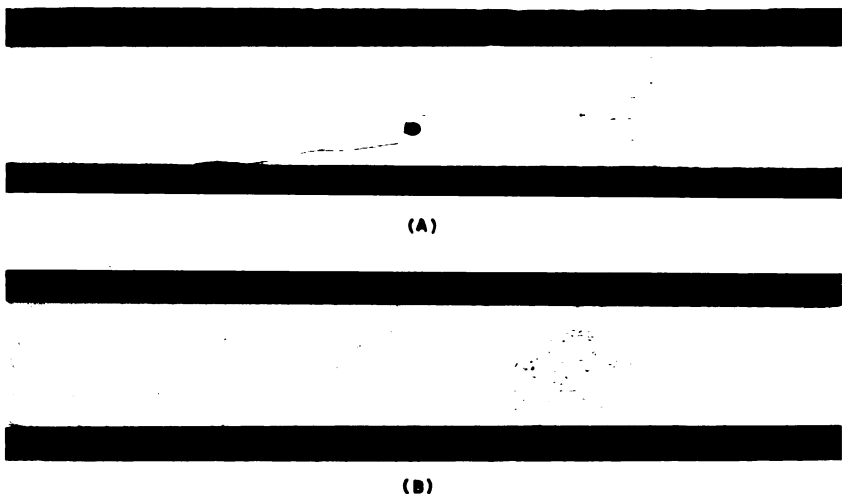


FIGURE 5.18. Zircaloy-Hafnium Welds Showing Effect of Position of Weld Pass with Respect to Original Butt Seam on Weld Bead Configuration: (a) Electrode On-Seam; (b) Electrode $\frac{1}{16}$ – $\frac{1}{32}$ In. on Hafnium Side of Seam.

Hoge concluded that the welds were as strong as the component parts at room temperature. At room temperature, the specimens necked down and fractured in the hafnium side of the weld. At 200° F there was no necking, but the specimens still broke in the hafnium. At 400 and 500° F, however, fracture occurred in the Zircaloy-2 side of the weld.

Hoge's work on hafnium-Zircaloy-2 welds suggested that stronger welds might be realized at 400 to 500° F if the amount of hafnium in the weld alloy could be increased. This can be accomplished by directing the arc on the hafnium side of the joint. The effect of welding $\frac{3}{32}$ inch off the joint on the weld bead configuration is illustrated in Figure 5.18. The tensile properties of welded specimens are presented in Table 5.8 as a function of the distance between the butt seam and the line of electrode travel. It is seen that only a moderate increase in yield strength is realized in the as-welded specimens by off-setting the weld bead. The major advantage of off-setting appears to be that of minimizing undercutting of the Zircaloy side of the weld. Hafnium-Zircaloy-2 welds are normally made $\frac{1}{16}$ to $\frac{3}{32}$ inch on the hafnium side of the seam.

Joint Design

The typical weld path along the length of a control rod is indicated by the heavy dark lines in Figure 5.14. The path is not exactly straight, as the arc attempts to maintain constant voltage

TABLE 5.8—ROOM TEMPERATURE MECHANICAL PROPERTIES OF HAFNIUM-ZIRCALOY-2 BUTT WELDS

| Weld position | 0.2 percent yield strength (×1000 psi) | Tensile strength (×1000 psi) | Total (%) elongation | R.A. (%) |
|--|--|------------------------------------|-------------------------|----------|
| On seam ¹ | | 75. 0 | 5 | 9 |
| ½ in. on hafnium side ¹ | 53. 8 | 76. 8 | 9 | 2 |
| ⅛ in. on hafnium side ¹ | 55. 6 | 78. 7 | 9 | 9 |
| ¾ in. on hafnium side ¹ | 58. 4 | 77. 9 | 9 | 5 |
| ½ in. on hafnium side ² | 19. 4 | 56. 5 | 12 | 23 |
| ½ in. on hafnium side ² | 20. 7 | 57. 7 | 12 | 25 |

¹ Specimens tested as welded and machined (160 amps, 16 volts, 6¼ in./min).

² Specimens tested after annealing at 1,700° F for 15 min (160 amps, 16 volts, 6¼ in./min).

by holding a constant arc length. Thus, any plate waviness, distortion during welding, or misalignment during tacking or machining causes the arc to wander. This difficulty is largely overcome by using two passes. The first pass smoothes out the discontinuities and produces slight penetration; the second pass deepens the penetration and smoothes out the initial irregular pass. A joint design for two-pass welding is illustrated in Figure 5.19. An indication of the strength and ductility of this type of weld has been demonstrated by applying a load across the blades and noting that the blade will break above the weld only after approximately 12,500 lb has been applied to a 2-inch long section.

When the joint is designed as illustrated in Figure 5.20, the edge labelled "B" guides the arc, and only one welding pass need be made. However, the root radius will be approximately ½ inch compared with the ⅝- to ⅞-inch radius experienced in the previously described design because of the extra material in the T section. Such a control-rod section can be pressed flat without fracture in the joint.

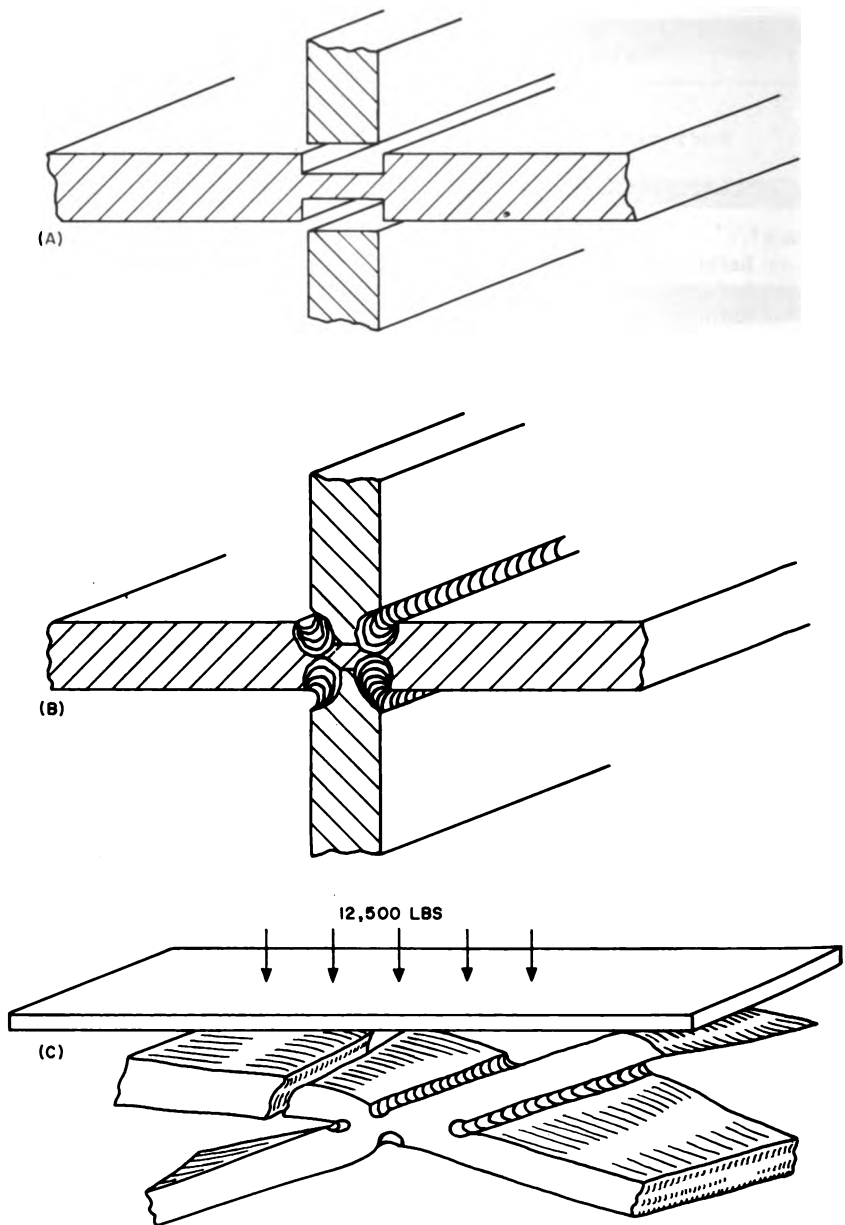


FIGURE 5.19. A Two-Pass Welding Joint Design for Fabricating Cruciform Shapes: (a) Component Design; (b) Weld Position; (c) Crush Test.

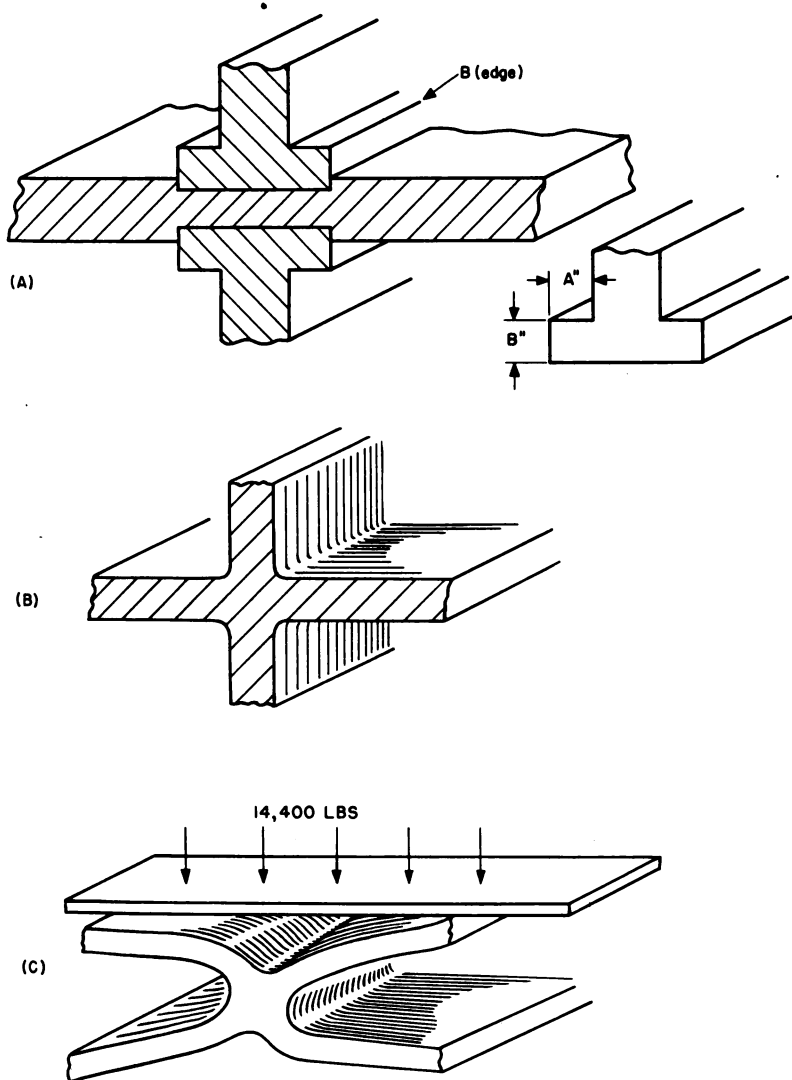


FIGURE 5.20. A Single-Pass Welding Joint Design for Fabricating Cruciform Shapes: (a) Component Design; (b) Weld Position; (c) Crush Test.

Corrosion Resistance of Welds

When components are properly prepared for welding and correct procedures are carefully followed, there is every reason to expect a product resistant to corrosion in high-temperature water. It is fortunate that all hafnium-zirconium alloys exhibit satisfactory corrosion rates in both steam and hot water. Small quantities of tungsten or nitrogen can enter into the weld pool and destroy the otherwise good corrosion-resisting properties of the weld alloy.

One type of corrosion is illustrated in Figure 5.21 as a thin line of

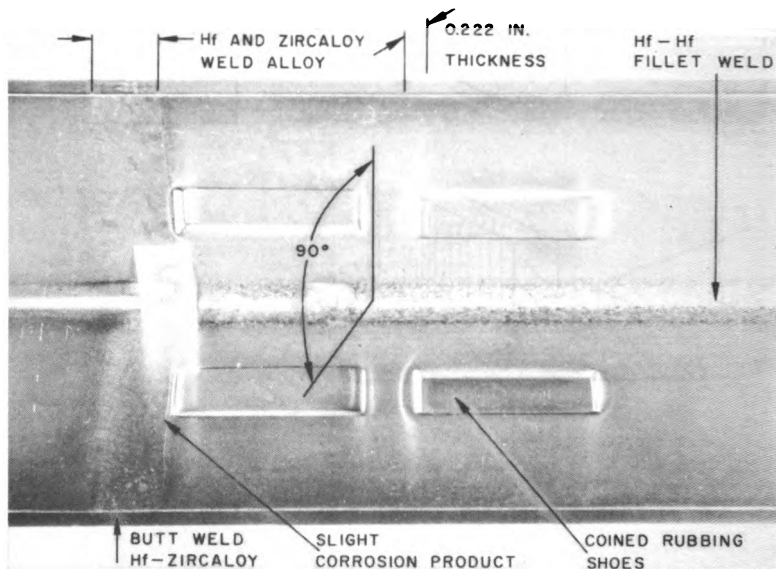


FIGURE 5.21. Corrosion Product at Butt Joint.

corrosion product at the butt joint. This corrosion product is the result of insufficient cleaning prior to welding and serves to emphasize the need for faultless cleaning and handling techniques.

Special Applications

Control-rod blades are generally provided with rubbing shoes which are intended to center the control rod in its channel. Since radioactive wear products from these rubbing shoes may be released into the reactor coolant, it is desirable to use a material which minimizes this tendency. For this reason, Zircaloy has been employed as a rubbing-shoe material. The rubbing shoes cannot be mechanically attached to the control rod because they might become detached during the movement of the rod. Also, if shoes made of

Zircaloy-2 or any other material with a low cross section were threaded through the control rod, a "neutron window" would be formed; i.e., if a small hole through the hafnium plate were filled with a material of low cross section, neutrons otherwise stopped by the hafnium could pass through. Therefore, welding techniques have been established for attaching Zircaloy-2 rubbing shoes to hafnium control rods. One effective welding method is a "puddling" technique.

The hafnium plates (0.2 to 0.3 inch thick) are prepared for the puddling operation by drilling 0.010-inch deep impressions directly opposite each other on both sides of the plate. After cleaning and degreasing, the plates are loaded into an inert-atmosphere welding box having a slightly positive pressure. A 1½-inch thick copper plate, drilled and chamfered to expose the drilled impressions in the hafnium plate, is clamped on each side of the plate to carry away the heat developed during the subsequent welding and to prevent distortion. A tungsten hand torch is used to strike an arc at the periphery of an impression at 90 to 100 amp and 16 volts. When a hafnium puddle appears, a 0.125- x 0.050-inch Zircaloy-2 strip or wire is fed into the pool. As soon as the puddling has been completed around the circumference of the impression, the current is raised to 100 to 110 amp, with the 16 volts remaining constant. The process is completed by continuing with a spiral movement toward the center of the impression. The plate is turned over, and the opposite side is given the same puddling treatment. The plate is then turned over again, and another Zircaloy layer is added to the first. This process is continued, using a 10-minute cooling time between passes until a shoe $\frac{3}{16}$ inch high and 1½ inches in diameter has been formed. The plates are allowed to cool, removed from the welding box and fixture, and straightened before the shoes are rough-machined and X-rayed. Prior to subsequent machining operations, the plates are vacuum-annealed 1 hour at 700° F for stress relief.

Samples taken from the finish-machined rubbing shoe contain approximately 16 w/o hafnium in the first 0.00 to 0.020 inch out from the surface of the hafnium plate. The hafnium content further decreases to about 13 w/o hafnium and 7 w/o hafnium at 0.020 to 0.030 inch, and 0.030 to 0.040 inch, respectively, from the plate surface.

Another method used to attach Zircaloy-2 rubbing shoes to the hafnium blades employs a resistance-welding technique. Zircaloy-2 buttons, positioned opposite each other on both sides of the hafnium plate, are resistance-welded in place. The buttons used are $\frac{3}{4}$ inch in diameter by $\frac{3}{8}$ inch thick, with a rounded surface (2-inch radius)

on one side. The flat side of the button conforms to the surface of the resistance die, and the rounded surface provides a small initial point of contact between the button and the plate. The rounded surface promotes a direct bond from center to edge of the button, and allows slight machining errors without lowering the quality of the bond.

A large heat input is necessary, because the hafnium plate rapidly conducts the heat away from the source. As a result, pulsation, cooling and heating cycles, and forging variations must be carefully controlled to accomplish a fusion of the metals before the Zircaloy-2 button reaches its melting temperature. Figure 5.22 shows how a

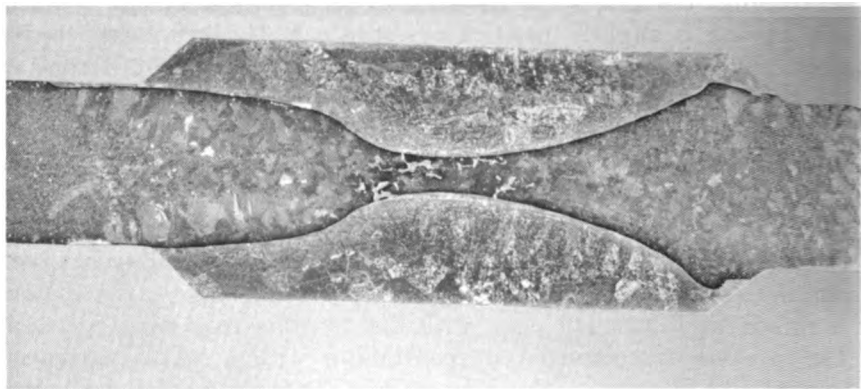


FIGURE 5.22. Cross Section of Zircaloy-2 Shoes Resistance-Welded to Hafnium.

Zircaloy-2 button is forged into the surface of the plate, causing a displacement of hafnium. This surface distortion is removed by machining after welding. The process must be closely controlled so that no internal contact between the two buttons occurs. If there is a point of contact, a neutron window will be formed. Figure 5.23 illustrates the metallurgical bond formed between Zircaloy-2 and hafnium in a typical resistance-welded rubbing shoe. An alternate type of rubbing shoe made by a coining operation on the hafnium portion of the rod is shown in Figure 5.21.

Joining of hafnium to titanium or zirconium may be accomplished by roll-bonding techniques [27]. Hafnium-titanium samples roll-bonded at temperatures ranging from 1,550 to 1,950° F to a total reduction of 67 percent (10 to 20 percent per pass) exhibit complete metallurgical bonding but fail at the bond line when subjected to a 90° bend test. Hafnium-Zircaloy-2 samples roll-bonded at temperatures of 1,550 and 1,750° F to a total reduction of 67 and 75 percent, respectively, exhibit apparent metallurgical bonding and satisfactorily withstand a 90° bend test but show bond failure when

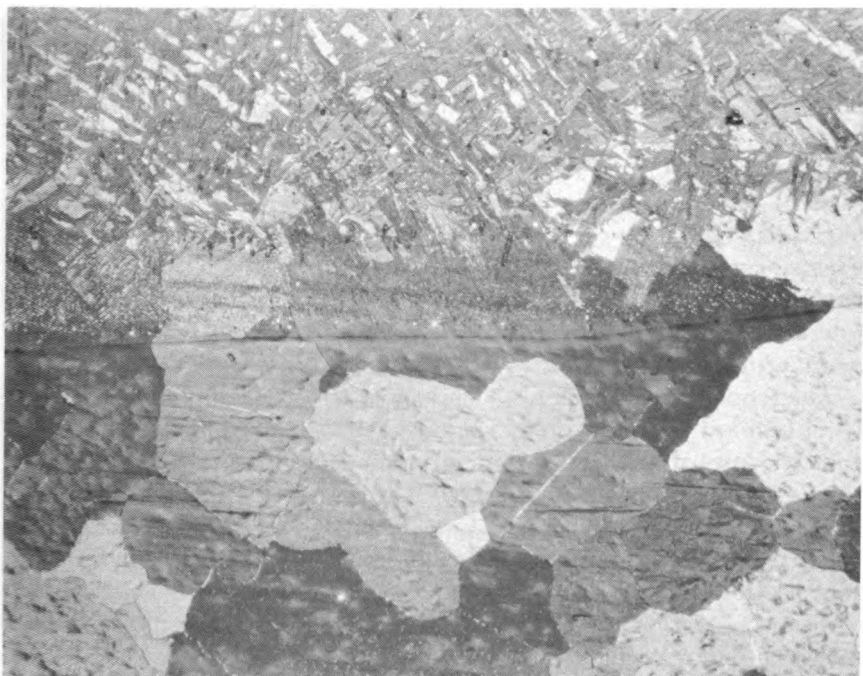


FIGURE 5.23 Hafnium-Zircaloy-2 Bond Taken from Sample Illustrated in Figure 5.22.

separation is attempted by a chisel test. It is believed that more suitable roll-bonded joints could be achieved by utilizing higher reductions, higher rolling temperatures, or by annealing after roll bonding.

5.8 MACHINING OF HAFNIUM

By H. B. Hunter ¹¹

General

Machined shapes of hafnium are easily obtainable using any of the conventional machine tools. Limited data pertaining to the machining of this metal indicate that its machining properties are similar to those of zirconium and its alloys. Some of the characteristics of both materials are as follows:

- (a) High rate of work hardening.
- (b) Tendency of material to gall and build up on the cutting edge.
- (c) Pyrophoric properties create a fire hazard during machining operations.

¹¹ Westinghouse Atomic Power Division.

(d) Abrasiveness of material, particularly the oxide, promotes tool wear.

To overcome these difficulties there are several actions which can be taken. Work hardening of the machined surface can be minimized by setting the depth of cut at 0.003 inch or greater and using sharp tools. At this depth the tip of the tool is cutting below the level of the layer of metal which was work hardened by the previous cut. [4] With a good clean cut, it is possible to maintain a corrosion-resistant surface comparable to a machined and pickled surface. This is an important point in that it permits, where close tolerances are required on finished parts, machining to final dimensions rather than pickling.

The tendency of material to build up on the cutting edge can also be minimized by frequent sharpening of the tool. It has been found that the use of carbide cutters gives a tool life of 10 to 20 times that of high-speed steel cutters. The use of water-soluble coolants has proved successful in producing good finishes and tool lives comparable to those obtained in the machining of stainless steel. In the face milling of hafnium plates experience has shown that a carbide-tipped shell cutter (Figure 5.24) can be used to mill 5,000 square inches to a depth of 0.020 inch before the cutter has to be sharpened. Machined surfaces of 63 μ in. rms or better are easily obtained if proper tool design and machining parameters are used.

Hafnium, like zirconium, when in a finely divided state such as fine machine chips, burns with intense heat when ignited. However, with the knowledge that the hazard does exist, precautions can be taken to enable the metal to be processed without danger to the operator, piece, or machine. It is strongly recommended that a coolant be directed at the chip-cutter interface. Chips should not be allowed to accumulate in the bed of the machine. The machine operator should continually remove the chips, particularly those under the cut, and store them in a closed container in order to minimize the fire hazard. Safe handling is discussed in detail in Appendix B of this volume.

The abrasive action of hafnium, and particularly of its oxide, decreases cutter life. Because of the cost and difficulty of reclaiming machine chips, minimum allowances are usually made on machining stock. This often results in decreased tool life because the uneven surface of the stock frequently causes the cutter to emerge from the metal and reimpinge on the oxide-contaminated surface. Removal of the oxide by sandblasting will improve tool life if the part has been previously hot worked. When high production can offset the increased cost, carbide-tipped cutters are recommended. Before con-

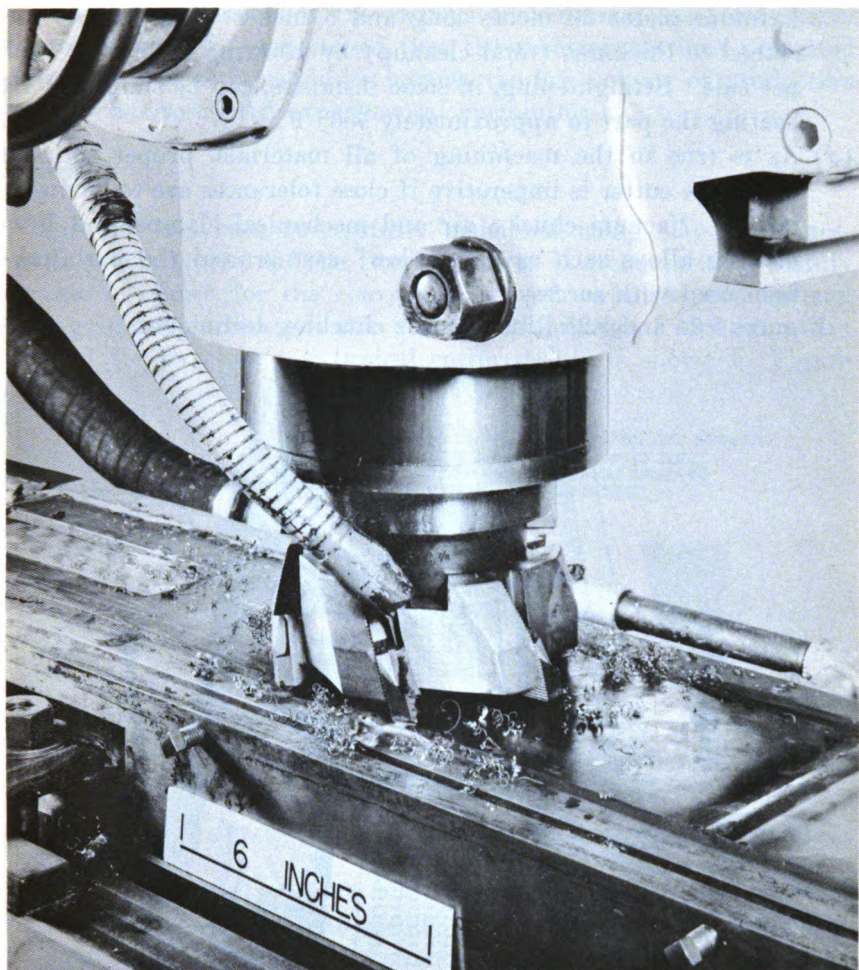


FIGURE 5.24. Milling Cutter and Plate Mounted on Vacuum Chuck.

sidering specific machining operations, a few generalities should be noted :

- (a) It has been found that the weld structure (beta-quenched) of hafnium machines the same as the wrought structure. The same is true of a fusion-weld joint between Zircaloy-2 and hafnium.
- (b) Tungsten inclusions resulting from the melting and welding techniques used present some machining problems, particularly in slab milling. The inclusion destroys the cutting edge of the tool. Furthermore, the collision of the cutter with the inclusion may cause a spark which may ignite machining chips.
- (c) To minimize the allowance for machining stock, the part should be straightened by pressing and detwisting. As an example,

hafnium plates 50 inches long and 5 inches wide can be machined to thickness (total cleanup) by allowing only 0.010 inch per side. Straightening, in some instances, can be simplified by heating the part to approximately 500° F.

- (d) As is true in the machining of all materials, proper support under the cutter is imperative if close tolerances are to be maintained. Vacuum chucks, air and mechanical clamps, and low-melting alloys such as "Cerro-low" cast around the part have been used with success.

Figures 5.24 and 5.25 illustrate the chucking techniques.

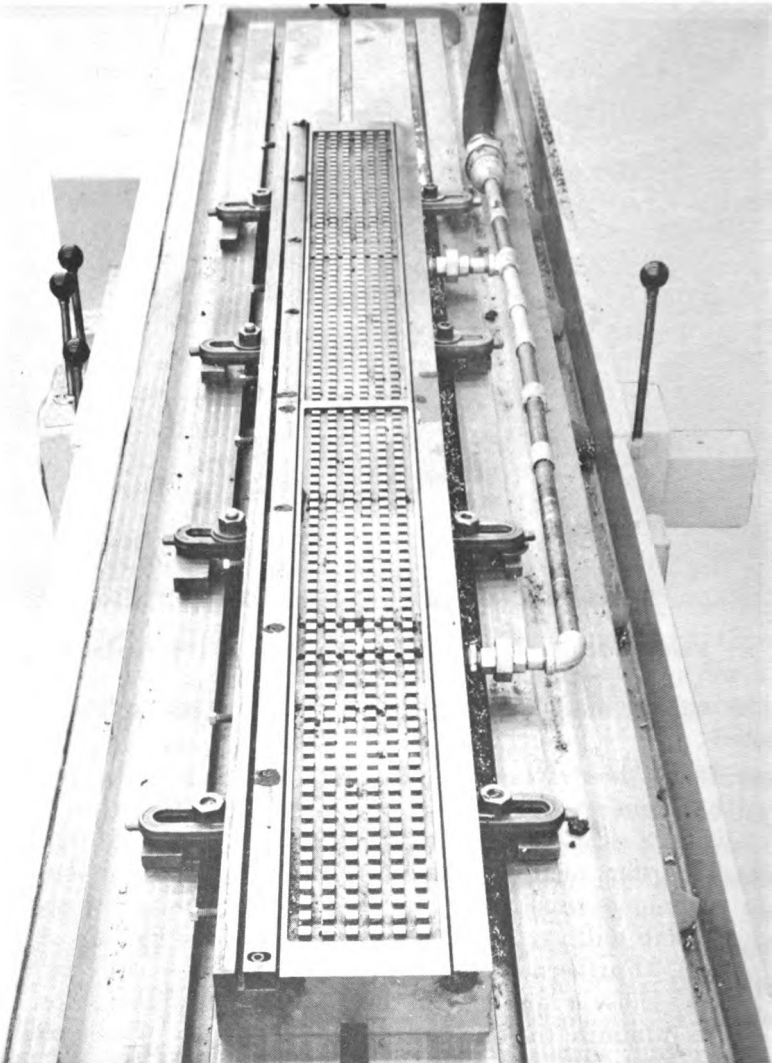


FIGURE 5.25. Vacuum Chuck for Face Milling Hafnium Plate.

Before a discussion of the various conventional machining techniques, it must be emphasized that the recommendations presented should be used only as guides because the low volume of production activity has restricted experimental machining.

Milling

Hafnium has been successfully machined using slab- and face-milling techniques. Of the two, the latter is recommended, mainly because it allows for the convenient use of carbide-tipped cutters. Any grade of carbide suitable for the machining of aluminum can be used for hafnium. A typical cutter design is shown in Figure 5.26.

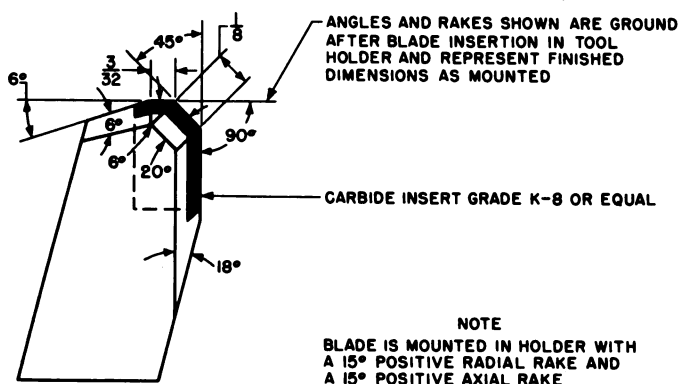


FIGURE 5.26. Face Mill Cutting Blade Rake and Angles for Machining Hafnium.

Milling speeds between 100 and 200 surface feet per minute, with a feed of 2 to 3 inches per minute, and cutting depths of 0.005 to 0.030 inch have been used successfully in producing a finish of 63 μ in. rms or better. Heavier cuts and faster speeds could be used; however, the fire hazard increases as the chip temperature increases.

One of the main disadvantages of slab-milling is the damage to the work when a cutting edge is chipped by a tungsten inclusion. When this occurs, a scarred surface appears on the piece from the point of the inclusion to the end of the cut. If slab milling has to be performed and there are a large number of pieces, the use of carbide-tipped slab-milling cutters may be warranted. These would probably prove successful, as they have in the machining of zirconium and Zircaloy. Their advantage is appreciably longer tool life than that obtained from tool-steel cutters. If slabbing is required, climb-milling is preferred in that it minimizes the work-hardening effect and gives longer tool life.

The use of the conventional end mills has been proven satisfactory. Frequent sharpening is required for best results.

Turning and Boring

Most of the information on the machining of hafnium deals with milling operations. However, there is little doubt that turning and boring could be successfully performed using machining parameters suitable for zirconium.

| <i>Operation</i> | <i>SFM</i> | <i>Feed (in./revolution)</i> |
|------------------|-----------------|------------------------------|
| Turning..... | 100 to 150..... | 0.005 to 0.015 |
| Boring..... | 40 to 80..... | 0.005 to 0.010 |

Miscellaneous Operations

Miscellaneous operations such as drilling and tapping are easily performed on hafnium using standard techniques and equipment. A drilling speed of approximately 50 SFM at a feed of 0.005 inch per revolution is recommended.

Shearing of hafnium up to $\frac{1}{4}$ -inch thickness has been accomplished with limited success. At room temperature, shattering of the sheared edge is prevalent, particularly in the direction of rolling. This can be minimized by shearing at a slightly elevated temperature (approximately 500° F). A blade clearance of 0.008 inch for $\frac{1}{4}$ -inch thickness has been used.

Band sawing of hafnium ($\frac{1}{4}$ inch thick) has also presented problems because of its abrasive property. While the sawing of zirconium has been successful using blades with 10 teeth per inch at slow speeds, it has not been satisfactorily done with hafnium. Because of this difficulty, slitting saws on milling machines and abrasive cut-off wheels (Crystolon abrasive, 120-grit, rubber-bonded) have been used to better advantage. With the cut-off wheel, it must be remembered that the sludge presents a fire hazard and should be treated accordingly. Even though the particles of metal are probably oxidized during the cut and the sludge is moist, there is always a possibility that finely-divided hafnium powder, which is easily ignited, is being dispersed.

5.9 PICKLING OF HAFNIUM

By S. Kass¹²

General

The excellent resistance of hafnium to corrosion in water and steam at elevated temperatures is not always evident on the surfaces of fabricated components without prior surface treatment and clean handling. A truly representative surface on good-quality material

¹² Westinghouse Atomic Power Division.

corrodes at a very low rate with the formation of a temper film of oxide, while a poor surface on the same material corrodes at a more rapid rate with the formation of a dull gray or loose white oxide. Thus, care must be exercised in surface preparation if spurious results are to be avoided. It should be noted that although hafnium behaves much like zirconium in this respect, it is less sensitive to surface preparation than zirconium.

Operations such as rolling, extruding, machining, and abrading produce a layer of disturbed and contaminated metal at the surface. The affected layer exhibits more rapid corrosion rates than the bulk metal, but this layer may be removed readily by chemical etching. The amount of surface metal which must be removed in order to produce a corrosion-resistant surface is dependent upon the history of the component. Cold rolling, hot rolling, extruding, machining, abrading, etc., result in varying depths of surface contamination; therefore, different amounts of surface metal must be removed to reach unaffected metal.

Hydrofluoric acid solutions have been used for etching hafnium; however, the rate of surface-metal removal is erratic and highly dependent upon temperature. Often a reaction-product smut forms on the surfaces. For these reasons, etching is performed in modified fluoride baths containing nitric acid as described below.

Pre-Etching Cleaning

All dirt, oil, fingerprints, etc., must be completely removed from the surfaces prior to etching. Surface contamination such as this will result in nonuniform attack by the etchant. Oils, greases, and other surface contaminants are removed by degreasing. Trichlorethylene or perchlorethylene vapor degreasing is used to remove hydrocarbons, and alcohol immersion and/or wiping is used to remove perspiration and similar contaminants. Dirt is removed by detergent washing. The components are dried by evaporation or by blowing with filtered, dry, compressed air. Cleaned components are handled with clean, lint-free, cotton gloves. The surfaces of all items which come in contact with cleaned components are cleaned in a manner equivalent to that used on the component itself. Cleaned components are enclosed in clean containers or wrapped in either heavy paper or plastic to prevent surface contamination when not being processed.

Etching

Properly etched components are bright and shiny and exhibit no surface irregularities. A well-etched surface has a metallographic finish; i.e., the microstructure can be seen under a microscope.

While the terms "etching" and "pickling" have come into general use in connection with the process described here, it is actually a chemical polishing operation. The pickling bath composition and temperature may be varied slightly to control the rate of pickling as required by the complexity of the components. The components are generally supported on stainless steel (type 316 or 347) fixtures during the pickling. Fixtures coated with acid-resistant materials have also been successfully used. Care must be exercised in the design of the fixtures to minimize the stainless steel-to-hafnium contact in order to prevent areas of preferential etching at the contact points (rig marks). Prior to etching, the components are rinsed in tap water at the same temperature as the pickling bath to improve wetting action by the acid. A large ratio of etchant volume-to-component surface is desirable to minimize the temperature rise of the bath due to the exothermic reaction. Pickling at too-high temperatures often results in pitting and blistering. The components and the etchant should be agitated throughout the pickling operation to prevent preferential surface attack (rig marks, pitting, blistering, or erosion). Mechanical stirring should not be applied because of the severe cutting action which may occur. Agitation supplied by a fine stream of filtered air has proved satisfactory. The pickling can be accomplished by total or alternate immersion. The temperature of the pickling bath should be maintained between 80 and 120° F, preferably at the lower limit. Etching in excess of the upper limit results in pitted and blistered surfaces, while etching below the lower limit requires excessively long immersion times. The time required to remove a given amount of surface material is given in Figure 5.27.

Rinsing

Perhaps the most critical aspect of the pickling operation is the removal of all residual etchant from the component surfaces. Accelerated corrosion, characterized by the formation of loose, white corrosion product, is observed if the residual etchant is not completely removed from the surfaces or if the etchant is permitted to dry upon the surfaces. The component should be completely immersed in a tank containing tap water or a dilute nitric acid solution, and adequate agitation or flow must be provided for a minimum of 5 minutes. The parts are then transferred to a second tank, completely immersed, and rinsed until all traces of acid entrapment or contamination are removed. The components are then rinsed in hot (180° F), deionized water (100,000 ohm-cm minimum resistivity) to remove the final traces of the etchant or the tap water. The com-

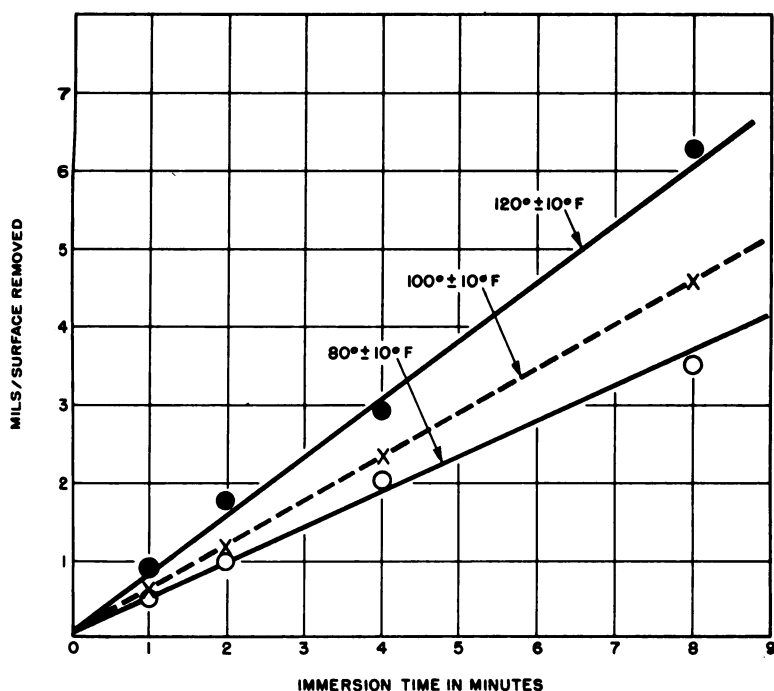


FIGURE 5.27. Effect of Temperature upon Rate of Metal Removal during Pickling of Hafnium.

ponents are dried by evaporation, by wiping with a clean, lint-free cloth, or by blowing with filtered, oil-free air. Pickled components are handled with clean, lint-free gloves. Components are enclosed in clean containers or wrapped in either heavy paper or plastic to prevent contamination when not being processed.

Typical optimum pickling solution specifications are shown in Table 5.9.

TABLE 5.9—BATH COMPOSITIONS (PERCENT BY VOLUME)

| | Bath A for simple shapes | Bath B for simple shapes |
|-------------------------------|-----------------------------|-----------------------------|
| HF (52%) | 3.6 | 2.5 |
| HNO ₃ (sp gr 1.42) | 39 | 39 |
| H ₂ O | Balance | Balance |

The bath can be operated for long periods of time and can be regenerated by the addition of hydrofluoric acid. As a general rule, $\frac{1}{2}$ pound of metal may be removed per gallon of etchant before the bath need be regenerated or changed. The pickling rates of hafnium in Bath "A" are shown in Figure 5.27.

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Chapter 6

HAFNIUM ALLOY SYSTEMS

By D. K. DEARDORFF,¹ O. N. CARLSON,² and H. KATO¹

6.1 INTRODUCTION

From considerations of the criteria usually examined in forecasting phase stability in binary alloys the alloying behavior of hafnium would be expected to be very similar to that of zirconium. The atomic sizes of the two elements are almost identical since the interatomic distances are identical to three significant figures. As the crystal structure and the valence are identical, the Brillouin zones and the shape of the Fermi surface should be almost identical. In the present state of knowledge it is not possible to predict the differences between the alloying behavior of the two metals. The principal differences between zirconium and hafnium constitutional diagrams should be those introduced by the higher melting point and elevated transformation temperature of hafnium.

Only five hafnium alloy systems are sufficiently well investigated to permit the presentation of phase diagrams. Two of these, the hafnium-thorium system and the hafnium-cobalt system, differ significantly from the corresponding zirconium systems. It thus appears that the subtle difference between the hafnium and zirconium atoms may be reflected in a considerably less subtle difference in their alloying behavior. An examination of the available information concerning the intermetallic phase or compound forming tendencies of the two metals reveals both similarities and differences. Both metals form carbides, borides, nitrides, and oxides of the same structure and stoichiometry, the lattice parameters of the compounds of hafnium being slightly smaller than those of the corresponding compounds of zirconium. Neither hafnium nor zirconium exhibit any intermetallic phase formations in their alloy systems with thorium, niobium, or titanium. In general, the indications are that corresponding compounds are found in the systems with germanium, molybdenum, nickel, silicon, tin, and tungsten although, in some cases, the investigations have not been suffi-

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² Iowa State College.

ciently complete to establish whether there is complete correspondence (e.g., in the case of silicon). A number of systems appear to lack correspondence. Thus, HfCu_2 is reported, but ZrCu_2 is not. The corresponding intermetallic phases HfMn_2 and ZrMn_2 are reported, but the former has the MgNi_2 structure, while the latter has the MgZn_2 structure. Similarly, the intermetallic phases HfV_2 and ZrV_2 are reported to have the MgCu_2 and MgZn_2 structures, respectively. In the hafnium-iron system, Hf_2Fe , HfFe , and HfFe_3 are reported to occur, whereas in the zirconium-iron system, only ZrFe_2 is reported. It does not appear that a definite analysis can be made of the relative alloying behavior of hafnium and zirconium until more thorough experimental investigations have been carried out. The reader is referred to two excellent discussions on zirconium alloy systems by Pfeil [1] and Smoluchowski [2].

The high melting point and high transformation temperature complicate the establishment of hafnium phase diagrams. The melting point of $2,222^\circ\text{C}$ is several hundred degrees higher than that of zirconium ($1,852^\circ\text{C}$) and titanium ($1,688^\circ\text{C}$) so that it is more difficult to establish the solidus and liquidus lines of the hafnium-rich alloys than it is for its lower-melting-point relatives. The transformation temperature of $1,760^\circ\text{C}$ is practically double that of titanium (862°C) and zirconium (880°C) so that establishment of maximum or minimum solubilities in the neighborhood of the alpha-beta transformation requires advanced metallographic laboratory techniques.

The deleterious effects of oxygen and nitrogen on alloys of this group are so well known that no discussion of alloys can be presented without a statement of their purity. In this case the unavailability of hafnium before about 1953 has kept the older literature singularly free of questionable diagrams such as those faced by titanium and zirconium investigators. Hafnium refined by the van Arkel-de Boer process has been used for most of the diagrams described in this chapter. The oxygen content was 0.03 to 0.05 percent and nitrogen was of the order of 0.007 percent. At this low impurity level the diagrams can be considered valid.

6.2 HAFNIUM-BORON

Glaser, Moskowitz, and Post [3] established the existence of compounds HfB and HfB_2 by X-ray diffraction analyses. They reported that HfB has a face-centered cubic structure of the NaCl (B1) type with $a_0 = 4.62 \pm 0.02\text{\AA}$ and the HfB_2 has a hexagonal structure isomorphous to ZrB_2 with $a = 3.14 \pm 0.002\text{\AA}$, $c = 3.470 \pm 0.002\text{\AA}$, and $c/a =$

1.105. The same workers also determined that HfB_2 melts at $3,250 \pm 100^\circ \text{C}$ and that it has a room-temperature resistivity of 12 microhm-cm. The melting point of a boride of undefined composition is about $3,100^\circ \text{C}$ [4].

6.3 HAFNIUM-CARBON

Most of the reported work on this system concerns the carbide, HfC . Agte and Alterthum [5] determined that the compound HfC melted near $3,900^\circ \text{C}$. Cotter and Kohn [6] reported the possible existence of a eutectic reaction between the carbide and carbon at $2,800^\circ \text{C}$. From X-ray diffraction analyses, they determined that the carbide was of the NaCl type with a lattice constant $a = 4.641 \pm 0.001 \text{ \AA}$. This agrees with the earlier work of Glaser, Moskowitz, and Post [3]. Hansen [7] gives references for additional determinations of $a = 4.70 \text{ \AA}$, $a = 4.467 \text{ \AA}$, $a = 4.635 \text{ \AA}$, $a = 4.6365 \text{ \AA}$.

6.4 HAFNIUM-CHROMIUM

Elliott [8] has identified HfCr_2 as isomorphous with MgNi_2 with $c = 16.325 \text{ kX}$, $a = 5.047 \text{ kX}$, and $c/a = 3.234$. The incipient melting temperature was determined as $1,480^\circ \text{C}$.

6.5 HAFNIUM-COBALT

A tentative phase diagram proposed by Dwight, Downey, and Nevitt [9, 10, 11, 12] is shown in Figure 6.1. These investigators report four intermetallic phases. Hf_2Co has the Ti_2Ni structure with $a_0 = 12.1036 \text{ \AA}$, HfCo has the CsCl structure with $a_0 = 3.165 \text{ \AA}$, and HfCo_2 has the MgCu_2 structure with $a_0 = 6.918 \text{ \AA}$. The fourth intermetallic phase, tentatively assigned the formula HfCo_6 , ranges from 85 to 88 a/o Co at $1,225^\circ \text{C}$ but apparently has a narrower existence range at lower temperatures. Its diffraction pattern is complex and has not been indexed. Elliott and Rostoker [13] had previously reported that an alloy of HfCo_2 exists and has the MgCu_2 type structure with a lattice parameter of 6.922 \AA . The incipient melting temperature was determined as $1,570^\circ \text{C}$.

6.6 HAFNIUM-COPPER

Elliott [14] found that the diffraction pattern of a nominal HfCu_2 alloy was not of the Laves type, but similar to patterns of the Ti-Cu and Zr-Cu systems. The existence of TiCu_2 and ZrCu_2 has not been confirmed by other investigators.

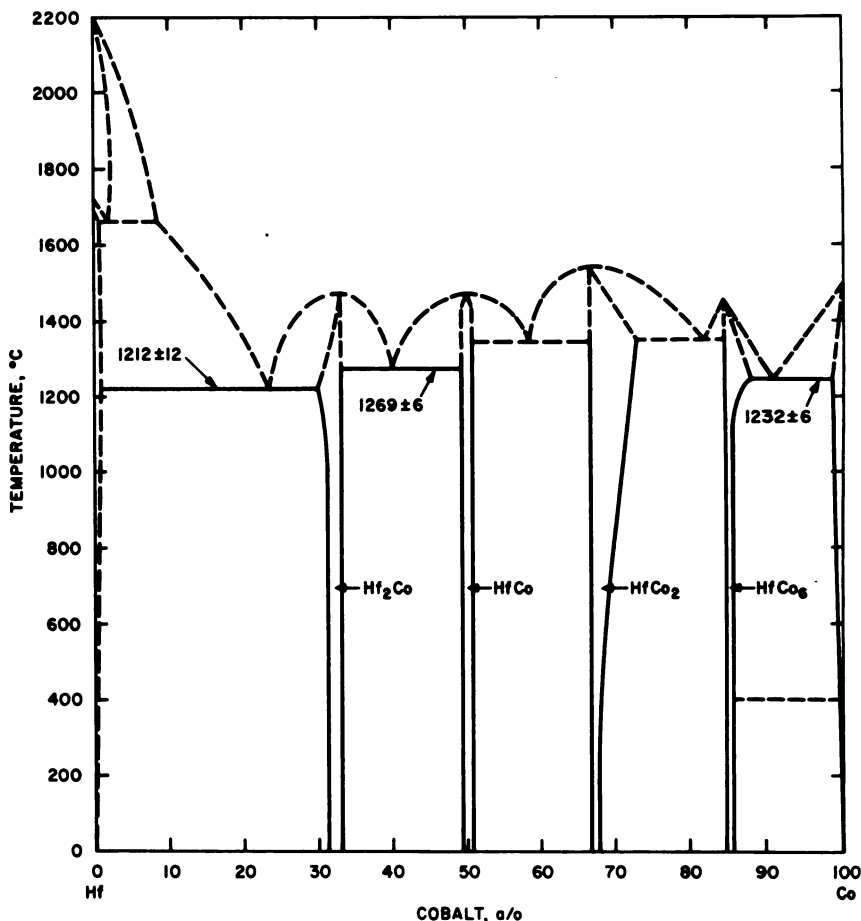


FIGURE 6.1. Hafnium-Cobalt Equilibrium Diagram.

6.7 HAFNIUM-GERMANIUM

One of intermediate phases of the hafnium-germanium system has been investigated by Smith and Bailey [15] who determined the structure of the compound HfGe_2 . It has an orthorhombic crystal structure and belongs to the space group D_{2h}^{17} -Cmcm. The lattice constants are $a=3.815\text{\AA}$, $b=15.004\text{\AA}$ and $c=3.7798\text{\AA}$.

6.8 HAFNIUM-HYDROGEN

Sidhu and McGuire [16] have made an X-ray crystallographic study of the hafnium-hydrogen system. The hydride phases were prepared by reacting hafnium (5% Zr) with molecular hydrogen at 700–800° C and measuring the amount of hydrogen pickup both

gravimetrically and volumetrically. Hafnium was found to form three hydrides at room temperatures; a deformed cubic, a face-centered cubic, and a face-centered-tetragonal phase. The deformed cubic phase was found to extend to a composition corresponding to $\text{HfH}_{1.53}$. The face-centered cubic phase exists over the range extending from $\text{HfH}_{1.53}$ to $\text{HfH}_{1.70}$. The tetragonal phase appears at $\text{HfH}_{1.8}$ – $\text{HfH}_{1.87}$ and extends to $\text{HfH}_{1.98}$. The phase limits were determined metallographically and by X-ray analysis. The crystallographic data for the hafnium used in this study along with the various hydrides are to be found in Table 6.1.

Subsequent to the X-ray studies of Sidhu and McGuire, the phase relationships in the Hf-H system over the temperature range 251–872° C were studied by Veleckis and Edwards [17] by means of equilibrium hydrogen pressure measurements. (The hafnium material used in this study contained 1 w/o Zr.)

TABLE 6.1—DATA ON HYDRIDES FORMED IN HAFNIUM

| <i>Metal or compound</i> | <i>Composition</i> | <i>Crystal structure</i> | <i>Lattice parameter (Å)</i> |
|------------------------------|---|--------------------------|---|
| Hf (5w/o Zr)..... | Hf (5w/o Zr)..... | Hex..... | $a_0 = 3.200$ $c_0 = 5.061$ $c/a = 1.58$ |
| Deformed cubic hydride..... | Hf to $\text{HfH}_{1.53}$ | Def. Cubic..... | $a_0 = 4.702$ $c_0 = 4.678$ $c/a = 0.995$ |
| f.c.c. hydride..... | $\text{HfH}_{1.53}$ to $\text{HfH}_{1.70}$ | f.c.c..... | $a_0 = 4.708$ |
| f.c. tetragonal hydride..... | $\text{HfH}_{1.8}$, $\text{HfH}_{1.87}$ to $\text{HfH}_{1.98}$ | f.c. tetragonal..... | $a_0 = 4.882$ $c_0 = 4.384$ $c/a = 8.89$ |

The measurements consisted of determining the pressure of hydrogen in equilibrium with the metal as a function of hydrogen content in the metal at constant temperature. The experimental data are plotted in Figures 6.2 and 6.3. For any given isotherm, the initial rise represents the region of solubility of hydrogen in hafnium. The plateaus indicate equilibrium of two solid phases, whereas the inflections evident in the curves of Figure 6.3, representing higher concentration of hydrogen in the metal, reveal the presence of a third phase. The compositions of the three phases, so indicated, are in agreement with the three solid phases in the Hf-H system located by Sidhu and McGuire. The limits of solid solubility are best seen in the log-log plots of pressure versus concentrations, Figures 6.4 and 6.5. The initial straight line portions of these curves have slopes of nearly two and indicate obedience to Henry's law and monatomic solution of hydrogen in hafnium. The study of Veleckis and Edwards was one of equilibrium and it is interesting to note that even at low temperature (251° C) equilibrium is achieved within a few hours, whereas only 10 minutes are required at tem-

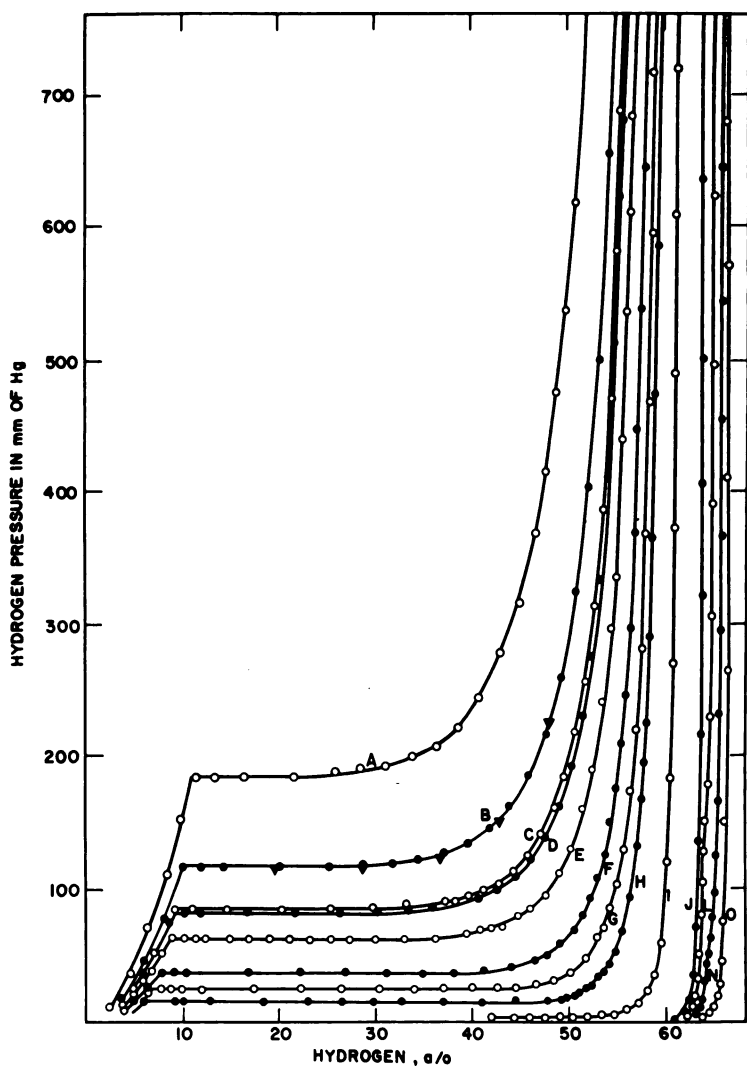


FIGURE 6.2. Pressure-Composition Isotherms for the Hydrogen-Hafnium System ($^{\circ}\text{C}$): A, 872 $^{\circ}$; B, 827 $^{\circ}$; C, 803.5 $^{\circ}$; D, 798.5 $^{\circ}$; E, 779 $^{\circ}$; F, 745 $^{\circ}$; G, 718 $^{\circ}$; H, 683 $^{\circ}$; I, 595 $^{\circ}$; J, 396.5 $^{\circ}$; L, 322 $^{\circ}$; N, 272 $^{\circ}$; O, 251 $^{\circ}$.

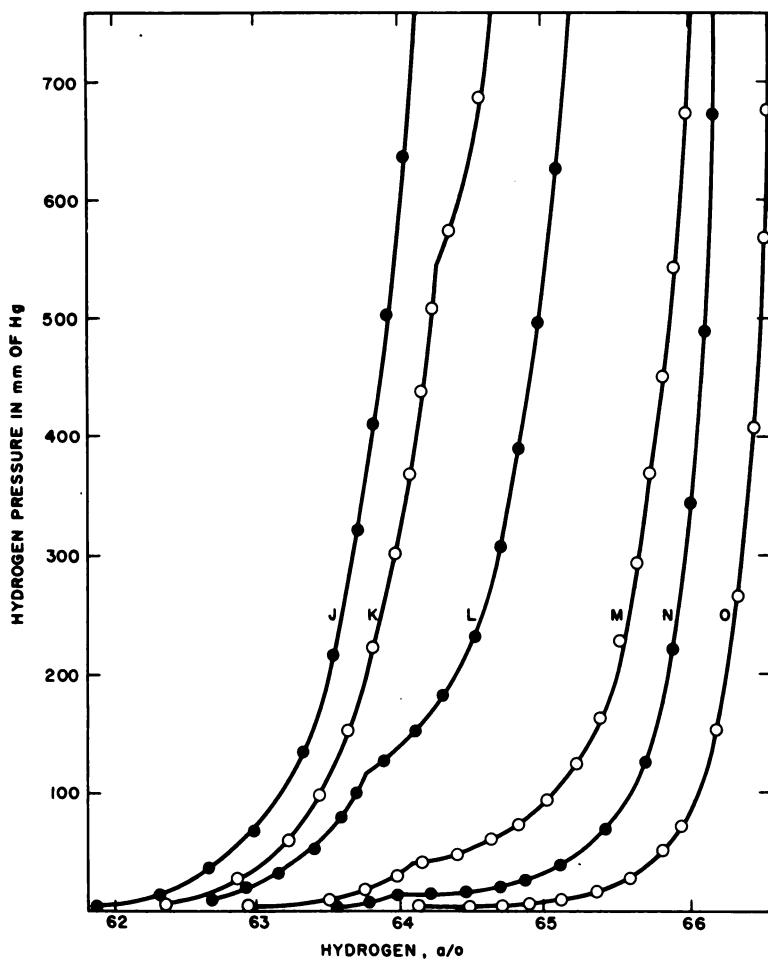


FIGURE 6.3. Pressure-Composition Isotherms for the Temperature Range 251 to 396.5°C: J, 396.5°; K, 365°; L, 322°; M, 298°; N, 272°; O, 251°.

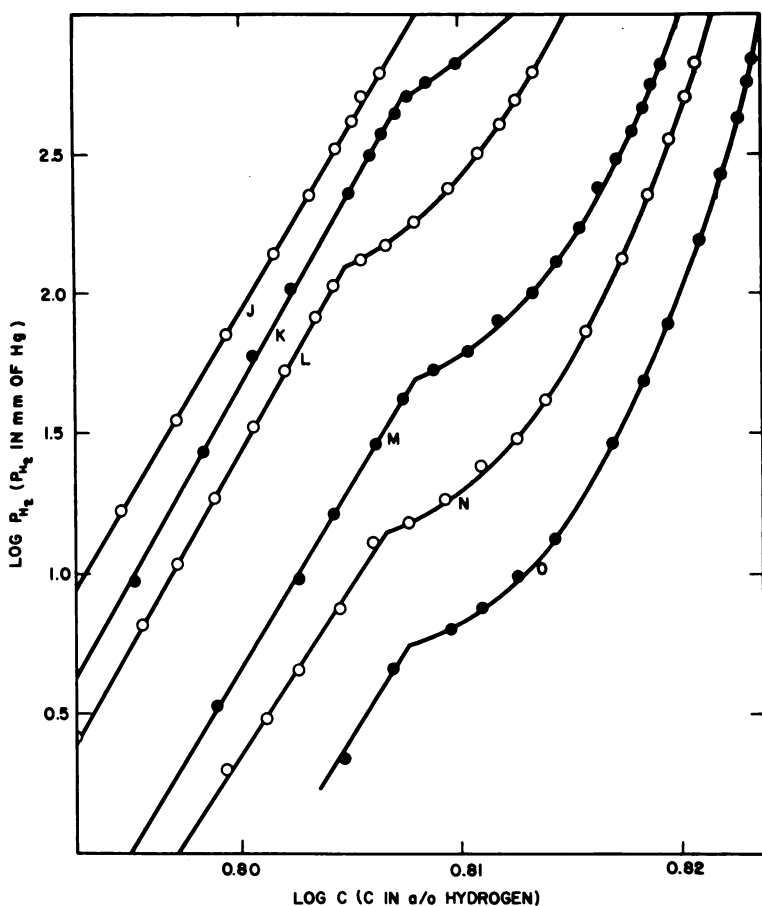


FIGURE 6.4. Log-Log Plot of Pressure-Composition Isotherms for the Temperature Range 251 to 396.5° C: J, 396.5°; K, 365°; L, 322°; M, 298°; N, 272°; O, 251°.

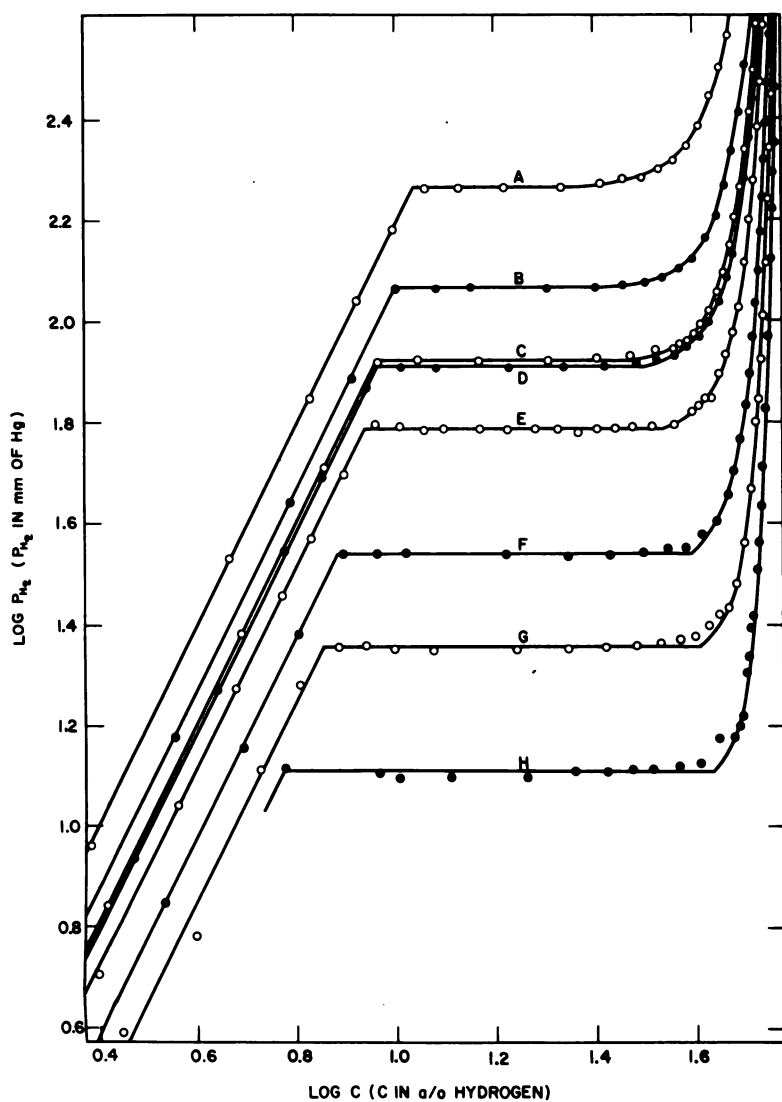


FIGURE 6.5. Log-Log Plot for Pressure-Composition Isotherms for the Temperature Range 683 to 872° C: A, 872°; B, 827°; C, 803.5°; D, 798.5°; E, 779°; F, 745°; G, 718°; H, 683°.

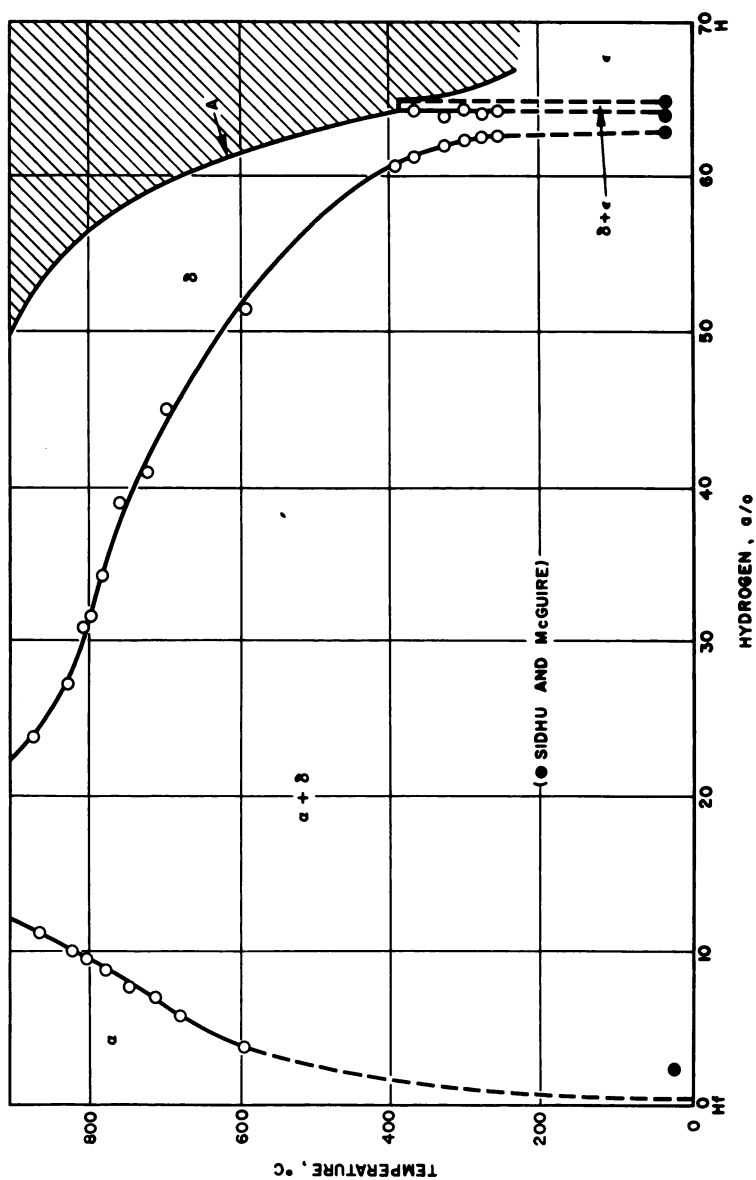


FIGURE 6.6. Hafnium-Hydrogen System.

peratures greater than 500° C. The rather rapid attainment to equilibrium was observed only for samples which had been pre-treated to remove the surface oxide barrier layer.

The compilation of most of the experimental results is contained in Figure 6.6. This figure represents projections upon the temperature-concentration plane of the solubility limits obtained from pressure-concentration isotherms. The curve labeled A gives the solubility of hydrogen in hafnium at a constant pressure of 760 mm of Hg. The shaded region remains unexplored. The boundary compositions are to be found in Table 6.2 which also has the approximate equilibrium pressures over the phases. The X-ray data of Sidhu and McGuire are also entered in the diagram of Figure 6.6. Thermodynamic calculations pertinent to the Hf-H system can be found in Chapter 9.

TABLE 6.2—BOUNDARY COMPOSITIONS OF THE VARIOUS REGIONS IN THE HYDROGEN-HAFNIUM SYSTEM

| Temperature (° C) | Phase boundary | | | | |
|-------------------|--------------------------|-----------------------|--------------------------|-----------------------|----------------------------|
| | $\alpha-(\alpha+\delta)$ | | $(\alpha+\delta)-\delta$ | | $\delta-(\delta+\epsilon)$ |
| | Conc ¹ | Pressure ² | Conc ¹ | Pressure ² | Conc |
| 871.9 | 10.89 | 183 | 24.0 | | |
| 826.8 | 10.07 | 116 | 27.4 | | |
| 803.8 | 9.27 | 83 | 31.0 | | |
| 798.5 | 9.14 | 81 | 31.6 | | |
| 779.4 | 8.67 | 61 | 34.5 | | |
| 745.2 | 7.69 | 35 | 39.3 | | |
| 717.8 | 7.18 | 23 | 40.7 | | |
| 682.7 | 6.00 | 13 | 45.7 | | |
| 594.8 | 3.61 | 1.7 | 51.5 | | |
| 396.5 | | | 60.6 | | |
| 365.1 | | | 61.0 | 550 | 64.3 |
| 322.0 | | | 61.5 | 110 | 63.8 |
| 297.9 | | | 62.0 | 20 | 64.3 |
| 271.6 | | | 62.5 | 10 | 64.1 |
| 250.7 | | | 63.0 | | 64.3 |

¹ Concentration of hydrogen, atom percent.

² Approximate pressure in mm of Hg.

6.9 HAFNIUM-IRON

The salient features of this diagram investigated by Hayes and Deardorff [18] are as follows:

1. Compounds HfFe and HfFe_3 melting at $1,540^\circ \text{C}$ and $2,120^\circ \text{C}$ respectively.
2. A hafnium-rich eutectic at 94 w/o Hf-6 w/o Fe and $1,280^\circ \text{C}$.
3. An iron-rich eutectic at about 95 w/o Fe-5 w/o Hf and $1,525^\circ \text{C}$.

Nevitt, Downey, and Morris [19] report the intermetallic phase Hf_2Fe and that it exhibits the Ti_2Ni structure with $a=12.0555 \text{ \AA}$.

6.10 HAFNIUM-MAGNESIUM

Hansen [20] reports that Hf and Mg do not alloy in the solid state. There may be considerable liquid solubility based on the analogy to titanium and zirconium.

6.11 HAFNIUM-MANGANESE

HfMn_2 has been identified by Elliott [21] as isomorphous with MgNi_2 with lattice parameters of $c=16.334 \text{ kX}$, $a=5.006 \text{ kX}$, and $c/a=3.263$. The incipient melting temperature was determined as $1,585^\circ \text{C}$.

Nevitt, Downey, and Morris [19] report the intermetallic phase HfMn of the Ti_2Ni type having $a=11.812 \text{ \AA}$.

6.12 HAFNIUM-MOLYBDENUM

Two modifications of HfMo_2 are reported by Elliott [22]. The predominant MgNi_2 type modification has lattice constants of $c=17.312 \text{ kX}$, $a=5.330 \text{ kX}$, and $c/a=3.248$. An additional high temperature modification was indicated which has the MgCu_2 type structure with $a=7.562 \text{ kX}$. The incipient melting temperature was in excess of $2,300^\circ \text{C}$.

6.13 HAFNIUM-NICKEL

The existence of hafnium-nickel compounds, Hf_2Ni , HfNi , Hf_2Ni_3 , HfNi_2 , and HfNi_4 was determined by Deardorff [23] through X-ray diffraction studies. Also observed were eutectic reactions near $1,200^\circ \text{C}$ at approximately 10 w/o and 70 w/o Ni compositions.

Elliott [24] reports that a nominal HfNi_2 alloy melted near $1,790^\circ \text{C}$ and that its diffraction pattern was similar to that of TiNi_3 .

Dwight [12] reports that HfNi_5 exhibits the AuBe_5 structure with a lattice parameter $a=6.683 \text{ \AA}$.

6.14 HAFNIUM-NIOBIUM

Duwez [25] made some X-ray diffraction analyses of hafnium-niobium alloys that had been quenched from $1,000^{\circ}\text{C}$. He reported that only body-centered cubic structures were found for alloys containing more than 30 a/o niobium, and both cubic and hexagonal structures were found for alloys containing less than 30 a/o niobium. Because the lattice parameters of the 30 to 100 a/o niobium alloys decrease uniformly with increasing niobium content, Duwez logically asserted that a solid solution existed at $1,000^{\circ}\text{C}$ between the composition limits of 30 to 100 a/o niobium. Elliott [26] found that the diffraction pattern of a nominal HfNb_2 alloy annealed at 800°C showed evidence of both cubic and hexagonal structures. There is too little data to define the system, but they are not inconsistent with a diagram of the type exhibited by zirconium-niobium.

6.15 HAFNIUM-NITROGEN

According to Hansen [27], the compound HfN has a metallic character, melts at $3,310^{\circ}\text{C}$, and has a face-centered cubic structure with $a = 4.52 \pm 0.02\text{\AA}$.

6.16 HAFNIUM-OXYGEN

Curtis, Doney, and Johnson [28] investigated the compound HfO_2 and reported the following lattice constants: $a = 5.11\text{\AA}$, $b = 5.14\text{\AA}$, $c = 5.28\text{\AA}$, and $\beta = 99^{\circ}44'$. The melting point is reported as $2,900^{\circ} \pm 25^{\circ}\text{C}$, and the inversion from monoclinic to tetragonal is reported to occur near $1,700^{\circ}\text{C}$. The inversion is accompanied by a calculated 3.4 percent theoretical density increase in contrast to the 7.5 percent increase reported for zirconia.

The investigators also report that the oxide forms only one compound each with silica and lime, $\text{HfO}_2 \cdot \text{SiO}_2$ and $\text{HfO}_2 \cdot \text{CaO}$, respectively. On the basis of X-ray diffraction investigations, they concluded that HfO_2 and ZrO_2 form a continuous series of solid solutions at about $1,800^{\circ}\text{C}$.

6.17 HAFNIUM-PLATINUM GROUP METALS

There is not enough information available to establish any of the phase diagrams of hafnium with the metals of the platinum group. However, a number of intermetallic phases have been identified as shown in Table 6.3.

TABLE 6.3 INTERMETALLIC PHASES FORMED BY HAFNIUM WITH THE PLATINUM GROUP

| Formula | Prototype | Lattice Parameters (Å) | | | Reference |
|--------------------|--------------------|------------------------|----------|--------|-----------|
| | | c | a | c/a | |
| HfRu | CsCl | ----- | 3. 225 | ----- | 11 |
| Hf ₂ Rh | Ti ₂ Ni | ----- | 12. 3255 | ----- | 10 |
| HfRh ₃ | Cu ₃ Au | ----- | 3. 911 | ----- | 29 |
| HfPd ₃ | TiNi ₃ | 9. 192 | 5. 595 | 1. 643 | 29 |
| HfRe ₂ | MgZn ₂ | 8. 595 | 5. 249 | 1. 637 | 12 |
| HfOs | CsCl | ----- | 3. 239 | ----- | 11 |
| HfOs ₂ | MgZn ₂ | 8. 491 | 5. 194 | 1. 635 | 12 |
| Hf ₂ Ir | Ti ₂ Ni | ----- | 12. 352 | ----- | 10 |
| HfIr ₃ | Cu ₃ Au | ----- | 3. 935 | ----- | 29 |
| Hf ₂ Pt | Ti ₂ Ni | ----- | 12. 461 | ----- | 10 |
| HfPt ₃ | TiNi ₃ | 9. 208 | 5. 636 | 1. 634 | 29 |

6.18 HAFNIUM-SILICON

Post, Glaser, and Moskowitz [30] established the existence of phases HfSi and HfSi₂ by X-ray diffraction and report the following lattice constants: HfSi has a hexagonal crystal structure with $a=6.86\text{Å}$, $c=12.60\text{Å}$, and $c/a=1.84$; and HfSi₂ has an orthorhombic structure with $a=3.67\text{Å}$, $b=14.56\text{Å}$, and $c=3.64\text{Å}$. X-ray diffraction analyses on HfSi₂ by Cotter, Kohn, and Potter [31] and by Smith and Bailey [15] agree with the foregoing. Hansen [32] states that the HfSi pattern needs corroboration and that the compound Hf₅Si₃ exists.

6.19 HAFNIUM-TANTALUM

Elliott [33] reports both cubic and hexagonal structures were present in a nominal HfTa₂ alloy annealed at 800° C. This system is probably similar to Ti-Ta and Ti-Nb.

6.20 HAFNIUM-THORIUM

The binary phase diagram for the hafnium-thorium system, shown in Figure 6.7, is the result of an investigation by Gibson, Loomis, and Carlson [34]. There is a eutectic reaction which occurs at 1,450° C and 25.7 w/o Hf. A eutectoid reaction occurs at 1,295° C and 8.9 w/o Hf, and an inverse peritectic reaction is postulated at 1,600° C and 96 w/o Hf.

The solid solubility limit of hafnium in alpha-thorium at temperatures below 650° C has been estimated at less than 5.0 w/o Hf. The solubility of thorium in hafnium at room temperatures is considered to be negligible.

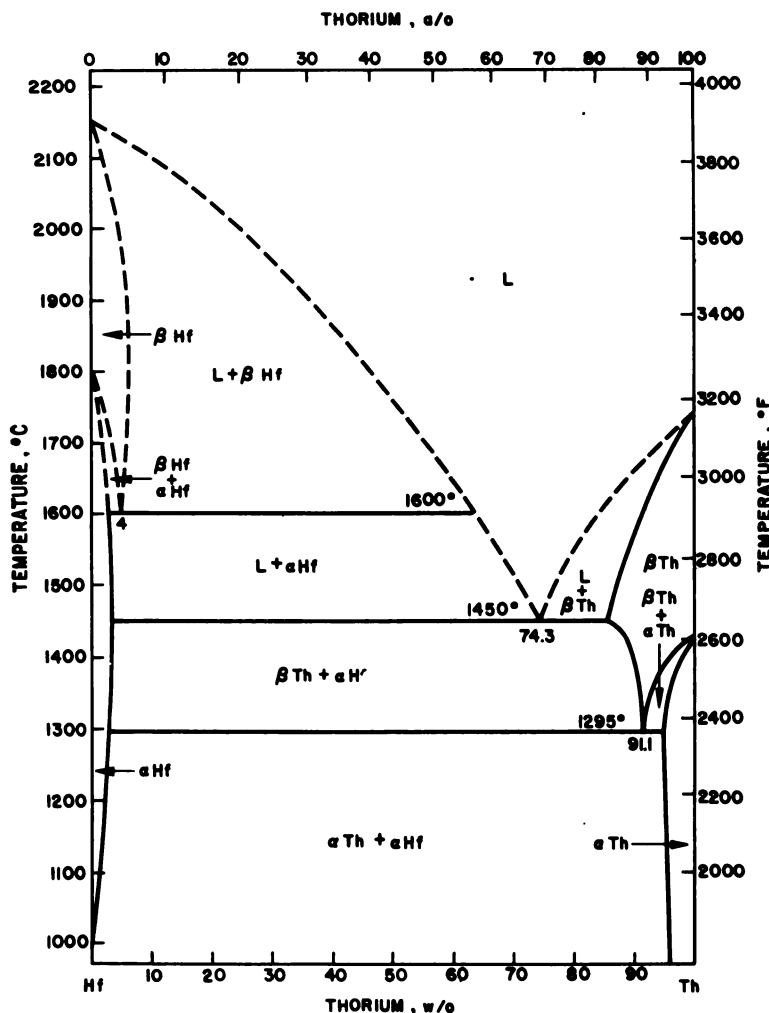


FIGURE 6.7. Hafnium-Thorium Phase Diagram (from Ref. 34 Courtesy of the American Society of Metals).

6.21 HAFNIUM-TIN

The structure of the compound Hf_5Sn_3 has been determined by Smith [31] from X-ray data on single crystals. The compound has the Mn_5Si_3 type structure and belongs to the space group $D_{6h}^3 - P6_3/\text{mcm}$. The lattice parameters are: $a = 8.418\text{\AA}$ and $c = 5.822\text{\AA}$.

6.22 HAFNIUM-TITANIUM

Hafnium and titanium are completely miscible both in liquid and solid states. The phase diagram developed by Deardorff and Hayes [36] is shown in Figure 6.8. Their determination of the solidus

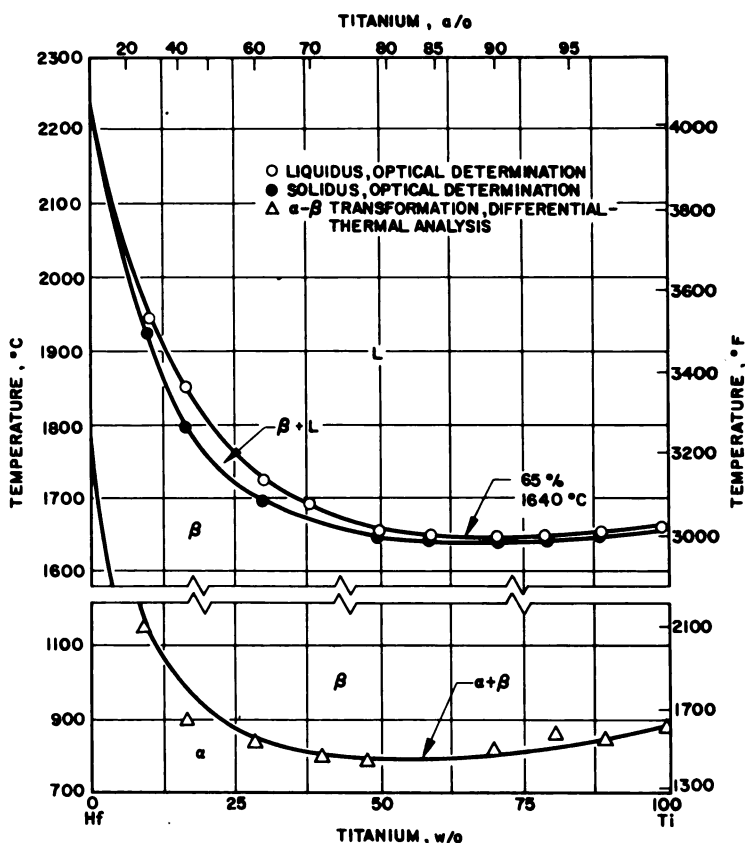


FIGURE 6.8. Hafnium-Titanium Equilibrium Diagram.

and liquidus curves were made by the use of a gradient-heating technique [37]. The alpha-plus-beta region, shown as a single line in the figure, was determined by use of a differential thermal analysis technique.

6.23 HAFNIUM-TUNGSTEN

Elliott [38] reports occurrence of HfW_2 , that it is isomorphous with MgCu_2 , and that its lattice parameter is $a = 7.556 \text{ kX}$. The work of Deardorff and Hayes [37] on melting point determination of hafnium indicates that hafnium and tungsten form a eutectic which melts around $2,030^\circ \text{C}$, but the composition of such a eutectic was not determined.

6.24 HAFNIUM-URANIUM

Peterson and Beerntsen [39] report the following results of an investigation of the hafnium-uranium alloy system recently completed. Melting point data show that uranium and hafnium are

soluble in all proportions in the high temperature, body-centered cubic form and exhibit a continuously sloping solidus between the melting points of the two elements.

Hafnium lowers the beta to gamma transformation of uranium by eutectoid formation at $733 \pm 2^\circ \text{C}$ and approximately 4.5 a/o hafnium. The maximum solubility of hafnium in beta uranium at the eutectoid temperature is less than 0.5 a/o hafnium. Thermal analyses indicate that hafnium raises the alpha-beta transformation of uranium by a peritectoid reaction. The transition temperature is increased from 662°C for the unalloyed uranium to $676 \pm 3^\circ \text{C}$ at approximately 0.2 a/o hafnium.

Alloys containing 20–65 a/o hafnium, quenched from $1,100^\circ \text{C}$, contain a hexagonal delta phase with $a=4.97\text{\AA}$ and $c=3.04\text{\AA}$. This phase appears to be metastable. Uranium lowers the alpha-beta transformation in hafnium to a monotectoid at about $1,150^\circ$ and 55 a/o hafnium. At $1,425^\circ \text{C}$, the solubility of uranium in hafnium is between 2.0 and 2.3 a/o.

6.25 HAFNIUM-VANADIUM

Elliott [40] reports the occurrence of HfV_2 , that it is isomorphous with MgCu_2 , and that its lattice parameter is $a = 7.371 \text{ kX}$. The incipient melting temperature was determined as $1,500^\circ \text{C}$.

6.26 HAFNIUM-ZIRCONIUM

The first diagram for the hafnium-zirconium system was published by Fast [41] and was based largely upon theoretical considerations. A diagram experimentally determined by Hayes and Deardorff [36] is shown in Figure 6.9. The diagram agrees closely with that of Fast's except for the location of the transformation temperature of hafnium. Hayes and Deardorff show a transformation temperature of $1,750^\circ \text{C}$, whereas Fast shows a value of $1,950^\circ \text{C}$. These values compare with the preferred values of $1,760 \pm 35^\circ$ for the melting point.

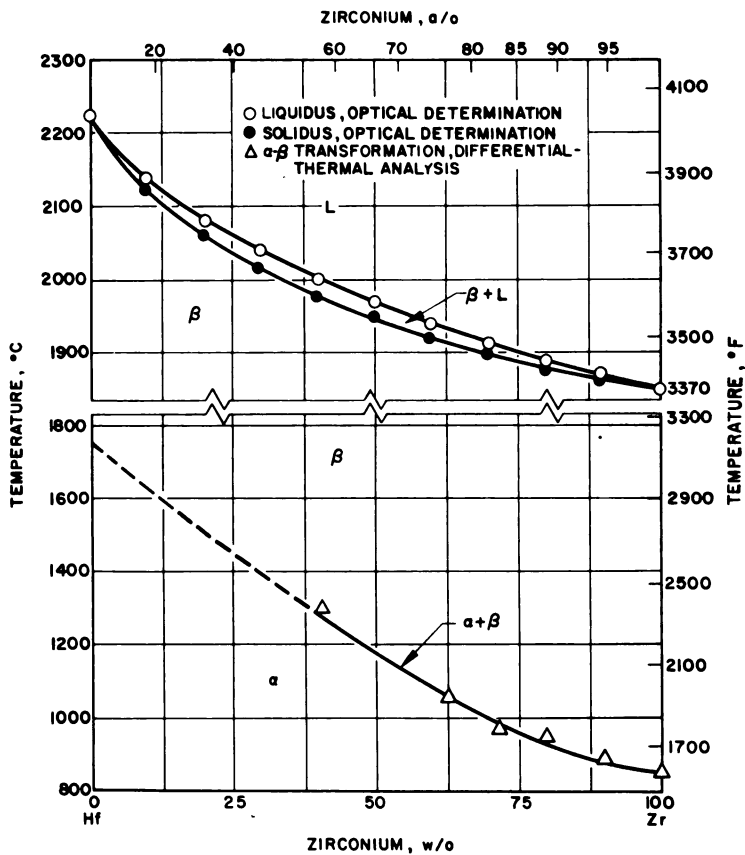


FIGURE 6.9. Hafnium-Zirconium Equilibrium Diagram.

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Chapter 7

PHYSICAL METALLURGY AND PROPERTIES OF HAFNIUM

K. M. GOLDMAN,¹ *Editor*

7.1 INTRODUCTION

There has been a reasonable amount of work done on the determination of many of the basic physical properties of hafnium. This, along with the moderate body of information which exists on its mechanical and corrosion properties, in addition to certain predictions of its properties and behavior which can be inferred from a knowledge of similar properties of zirconium and titanium, comprises the material for this chapter.

The sections concerning properties of hafnium include physical, atomic, and mechanical properties. Information on melting and boiling points, allotropic modifications, and electrical and thermal properties is presented. Nuclear properties are to be found in Chapter 1. Only the more basic chemical properties such as atomic number, atomic weight, and atomic radius are discussed. Chemical behavior in terms of reaction with liquids and gases is discussed in the corrosion section. The commonly reported mechanical properties, hardness, tensile, and creep, are included.

The discussion of the physical metallurgy of hafnium is necessarily limited because of the small quantity of information available. The topics on which some information is available include recrystallization, deformation textures, and metallography.

The corrosion section contains information on the reaction of hafnium with pressurized water and steam, solutions of acids, bases, and salts, and gases such as oxygen, steam, hydrogen, and nitrogen.

The purity of the materials used in many of the studies reported in the literature is frequently not specified. Zirconium as well as oxygen and nitrogen is often present in amounts sufficiently high to affect the properties being investigated. An attempt has been made to take into account the purity of the material in assessing the true nature of the properties discussed in the following pages.

7.2 PHYSICAL PROPERTIES OF HAFNIUM

By E. H. Roland ¹

It has only been in the past few years that hafnium of sufficiently high purity has been available to permit determination of reliable

¹ Westinghouse Atomic Power Division.

values of its physical properties. The most reliable values are summarized in Table 7.1, and each property is discussed in the succeeding portions of the chapter.

TABLE 7.1—PHYSICAL PROPERTIES OF HAFNIUM

| | |
|--|---|
| Melting point..... | $2,222 \pm 30^\circ \text{ C}$ |
| Boiling point..... | $3,100^\circ \text{ C}$ |
| Crystal structure..... | Close-packed hexagonal $a = 3.1883 \text{ \AA}$ $c = 5.0422 \text{ \AA}$ $c/a = 1.5815$ Body-centered cubic $a_0 = 3.50 \text{ \AA}$ |
| Allotropic transformation temperature..... | $1,760 \pm 35^\circ \text{ C}$ |
| Electrical resistivity at 25° C | $35.1 \times 10^6 \text{ ohm-cm}$ |
| Superconductivity transition temperature..... | $0.374 \pm 0.01^\circ \text{ K}$ |
| Coefficient of linear thermal expansion (20– 200° C)..... | $5.9 \times 10^{-6}/^\circ \text{ C}$ |
| Thermal conductivity at 50° C | $k = 0.223 \text{ watts/cm}^2 \text{ }^\circ \text{ C}$ |
| Density..... | $13.09 \pm 0.01 \text{ g/cm}^3$ |
| Thermal neutron absorption cross section..... | $105 \pm 5 \text{ barns}$ |
| Paramagnetic susceptibility (RT)..... | $(0.42 \pm 0.01) \times 10^{-6} \text{ emu/g}$ |
| Hall effect..... | $-0.16 \times 10^{-13} \text{ V cm/amp gauss}$ |
| Specific heat (25–100° C)..... | $6.25 \text{ cal/mol}^\circ \text{ C}$ |
| Atomic number..... | 72 |
| Atomic weight..... | 178.50 |

Melting Point

De Boer and Fast [1] in 1930 reported a value of $2,230 \pm 50^\circ \text{ C}$ for the melting point of hafnium. In this determination, the melting points of as-deposited iodide hafnium-zirconium alloys were extrapolated to 100 percent hafnium. Later measurements showed a wide difference in the melting point of hafnium as reported by different authors. McPherson, reported by Adenstedt [2], gave the melting point of hafnium as $1,975 \pm 25^\circ \text{ C}$. In McPherson's work, the hafnium specimen was suspended by a tungsten wire. Deardorff and Hayes [3], using a modified technique, report a value for the melting point of hafnium of $2,222 \pm 30^\circ \text{ C}$ and indicate a hafnium-tungsten eutectic reaction at $1,965^\circ \text{ C}$. The hafnium-tungsten eutectic temperature agrees closely with the $1,975^\circ \text{ C}$ value of the melting point reported by McPherson and probably explains this low value.

The best value appears to be $2,222 \pm 30^\circ \text{ C}$, reported by Deardorff and Hayes; as the samples employed had a lower impurity content than those reported by other investigators. The values and references for the melting point of hafnium are given in Table 7.2.

TABLE 7.2—THE MELTING POINT OF HAFNIUM

| <i>Melting point</i> | <i>Zr (w/o)</i> | <i>Reference</i> |
|----------------------|------------------------------|------------------|
| 2,230 ± 50° C | Extrapolated to 100% hafnium | 1 |
| 2,130 ± 15° C | 0.78 | 4 |
| 1,975 ± 30° C | 0.70 | 2 |
| 2,235 ± 5° C | Sponge hafnium | 5 |
| 2,222 ± 30° C | 0.0080 | 3 |

Boiling Point

The boiling point of hafnium has been calculated to be about 3,100° C by Oliver [6], and this value is also given in the ASM Metals Handbook [7]. Richardson [8] gives a value of 5,400° C. Richardson's value, however, is very likely that of HfO_2 rather than that of hafnium, for his was a determination by spectrographic means, and the sample was hafnia powder mixed with graphite powder. Unless the hafnia was actually reduced to hafnium, the 5,400° C figure refers to the boiling point of hafnia. There is also a possibility that a carbide of hafnium was formed.

Crystal Structure

The crystal structure of hafnium is close-packed hexagonal [9, 11, 12] up to about 1,760° C, above which the structure is body-centered cubic. The experimental values for the lattice constants of the hexagonal phase at room temperature are given in Table 7.3.

TABLE 7.3—LATTICE CONSTANTS OF HAFNIUM

| <i>a</i> | <i>c</i> | <i>c/a</i> | <i>w/o Zirconium</i> | <i>Reference</i> |
|----------|----------|------------|----------------------|------------------|
| 3.32 Å | 5.47 Å | 1.64 | Unknown | 11 |
| 3.206 Å | 5.068 Å | 1.581 | Unknown | 10 |
| 3.1883 Å | 5.0422 Å | 1.5815 | 0.78 | 4 |
| 3.1952 Å | 5.0569 Å | 1.5827 | 0.70 | 9 |
| 3.1991 Å | 5.072 Å | 1.586 | (Sponge) | 5 |

The values of $a=3.1952$ Å and $c=5.0569$ Å given by Duwez [9] appear to be the most reliable because the material contained a relatively small amount of zirconium. The early values are probably too high because of the higher zirconium and impurity content of the material available at that time.

Duwez [9] measured the lattice parameter of a series of hafnium-niobium alloys from 10 a/o niobium in hafnium to pure niobium. The samples were homogenized at 1,000° C for 48 hours and quenched to room temperature. Above 30 a/o niobium, the crystal structure was identified as body-centered cubic. Below 30 a/o niobium, the hexagonal hafnium phase was present as well as the body-centered cubic phase. By extrapolating to zero niobium concentration, a value of 3.50 Å is obtained for the lattice parameter of the body-centered

cubic modification of hafnium if it could be measured at room temperature.

Allotropic Modification

Hafnium has a close-packed hexagonal crystal lattice at low temperatures and a body-centered cubic structure at high temperatures. Zwikker [12] showed that the electrical resistance is a maximum at $1,327^{\circ}\text{C}$ and a minimum at $1,527^{\circ}\text{C}$, a behavior analogous to that of zirconium. Duwez [9] determined the transformation temperature to be $1,310 \pm 10^{\circ}\text{C}$, a value close to that reported by Zwikker. Fast [13], on the other hand, reported a value of $1,950 \pm 100^{\circ}\text{C}$, which is close to one of the melting point temperatures previously given.

To resolve this discrepancy, Deardorff and Kato [14] performed a resistometric determination of the effect of zirconium on the transformation temperature of hafnium. The temperatures (determined by an optical pyrometer) corresponding to the beginning of the transformation ranges of hafnium containing three different zirconium contents, 2.3, 9.3, and 18 a/o zirconium, were determined and were found to decrease linearly over this range of zirconium contents. The transformation temperature for pure hafnium, obtained by extrapolating to zero a/o zirconium, was found to be $1,760 \pm 35^{\circ}\text{C}$.

The value reported by Duwez [9], $1,310 \pm 10^{\circ}\text{C}$, was obtained by a rapid-cooling thermal analysis technique. Fast [13], about six months later, published the much higher value of $1,950 \pm 100^{\circ}\text{C}$. This value was based on Fast's own determination of $1,690^{\circ}\text{C}$ as the start of the transformation range for hafnium containing 5.7 a/o zirconium and also his belief that the hafnium which Duwez had used contained 19 a/o zirconium and that the $1,310^{\circ}\text{C}$ value should be associated with this composition. Fast assigned this 19 a/o zirconium to Duwez' hafnium because of the lattice parameters reported by Duwez. Russell [15], about a year later, stated that Duwez and Fast were probably reporting their lattice parameters in different units and reassigned a value of 6.0 a/o zirconium to Duwez' hafnium which corresponded to Fast's material. It is believed by Deardorff and Kato that Fast's work is essentially correct except that he probably should not have considered Duwez' $1,310^{\circ}\text{C}$ value in the extrapolation to his (Fast's) $1,690^{\circ}\text{C}$ number for his hafnium-5.7 a/o zirconium value. Deardorff and Kato believe that Duwez' $1,310^{\circ}\text{C}$ value was affected by fusion between the sample and the thermocouple.

Another value, $1,660^{\circ}\text{C}$, was determined by McGeary [16] by metallographic examination of heat-treated specimens. The zirconium content of this material is uncertain but is believed to be between 1 and 4 w/o.

The reported values of the alpha-beta transition temperatures are given in Table 7.4. The preferred value is that of Deardorff and Kato, $1,760^{\circ}\text{C}$. The transformation is unaffected by cooling rate [9] and, as in the case of zirconium and titanium, is a diffusionless type.

TABLE 7.4—SUMMARY OF ALPHA-BETA TRANSITION TEMPERATURE DATA

| Temperature | w/o Zirconium | Reference |
|-----------------------------------|-------------------------------|-----------|
| 1,327–1,527° C..... | Unknown..... | 12 |
| 1,950±100° C..... | 3..... | 13 |
| 1,310±10° C..... | 0.70..... | 9 |
| 1,760±35° C (preferred value).... | Extrapolated to 0 w/o Zr..... | 14 |
| 1,660° C..... | 1–4..... | 16 |

Electrical Resistivity

The electrical resistivity of hafnium has been measured by a number of investigators. The data obtained are summarized in Table 7.5 and are plotted in Figure 7.1. Much of the variation can be accounted for by differences of zirconium content and possibly other impurities.

Kurti and Simon [17], in 1935, employed magnetic cooling to measure the resistivity at low temperatures and showed that hafnium becomes superconducting at $0.35\pm0.05^{\circ}\text{K}$. However, Smith and Daunt [18] have reported a transition temperature of $0.374\pm0.01^{\circ}\text{K}$ for annealed hafnium, whereas unannealed hafnium shows no superconductivity down to 0.15°K . Roberts and Dabbs [19] found no evidence of superconductivity between 0.22°K and 4.18°K for

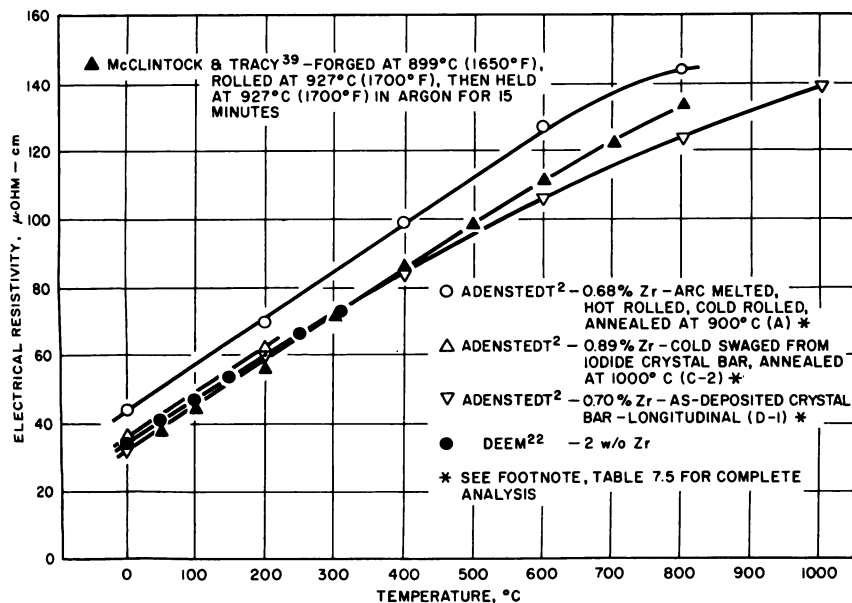


FIGURE 7.1. Electrical Resistivity of Hafnium.

material containing 5 w/o zirconium. The results for hafnium are tabulated in Table 7.6, where they are compared with those of zirconium and titanium.

TABLE 7.5—SUMMARY OF ELECTRICAL RESISTIVITY AND TEMPERATURE COEFFICIENTS OF RESISTIVITY OF HAFNIUM

| <i>Electrical resistivity</i> (μ ohm-cm) | <i>Temperature coefficient</i> ($^{\circ}\text{C}^{-1}\times 10^4$) | <i>Specimen history</i> | <i>Reference</i> | | |
|--|--|-------------------------|------------------|----------------|----------------|
| 30 at 0° C..... | 44..... | Unknown..... | 12 | | |
| 31.9 at 0° C | | | | | |
| 35.7 at 30° C..... | 39.8 (0–100° C)..... | Unknown..... | 21 | | |
| 29.6 at 0° C..... | | Unknown..... | 20 | | |
| 30 at 0° C..... | 44 (0–100° C)..... | Unknown..... | 1 | | |
| 43.9 at 0° C..... | 29.5 (0–200° C)..... | A..... | 2 | | |
| 69.8 at 200° C..... | 29.4 (0–800° C) | | | | |
| 98.8 at 400° C | | | | | |
| 127 at 600° C | | | | | |
| 147 at 800° C | | | | | |
| 41.4 at 0° C..... | | B..... | 2 | | |
| 36.3 at 0° C..... | | C-1..... | 2 | | |
| 35.7 at 0° C..... | 37.4 (0–200° C)..... | C-2..... | 2 | | |
| 62.4 at 200° C | | | | | |
| 32.7 at 0° C..... | 43.6 (0–200° C)..... | D-1..... | 2 | | |
| 61.1 at 200° C..... | 35.1 (0–800° C) | | | | |
| 84.4 at 400° C | | | | | |
| 106 at 600° C | | | | | |
| 124 at 800° C | | | | | |
| 139 at 1,000° C | | | | | |
| 32.0 at 0° C..... | 4.5 (0–200° C)..... | D-2..... | 2 | | |
| 34.1 at 0° C..... | | 2 w/o Zr..... | 22 | | |
| 40.6 at 50° F | | | | | |
| 47.1 at 100° C | | | | | |
| 53.6 at 150° C | | | | | |
| 60.1 at 200° C | | | | | |
| 66.6 at 250° C | | | | | |
| 36.6 at 25° C..... | | 1–4 w/o Zr..... | 16 | | |
| | Si | Al | Zr | O ₂ | N ₂ |
| A..... | 0.034 | 0.066 | 0.78 | 0.037 | 0.004 |
| B..... | 0.06 | 0.035 | 0.86 | 0.034 | 0.007 |
| C..... | 0.084 | 0.074 | 0.89 | | |
| D..... | 0.015 | 0.018 | 0.70 | | 0.002 |

A—Are melted, hot rolled, cold rolled, and annealed at 900° C.

B—Cold swaged from iodide crystal bar, cold swaged 20%, annealed at 1,000° C.

C-1—Cold swaged from iodide crystal bar.

C-2—Cold swaged from iodide crystal bar, annealed at 1,000° C.

D-1—As-deposited crystal bar—longitudinal.

D-2—As-deposited crystal bar—transverse.

TABLE 7.6—SUPERCONDUCTIVITY TRANSITION TEMPERATURES OF HAFNIUM, ZIRCONIUM, AND TITANIUM

| Element | Impurity | Transition temperature | Reference |
|---------|-------------------|--|-----------|
| Hf..... | Zr (unknown)..... | $0.35 \pm 0.05^\circ \text{K}$ | 17 |
| Hf..... | 0.9 w/o Zr..... | $0.374 \pm 0.01^\circ \text{K}$ | 18 |
| Hf..... | 5.0 w/o Zr..... | No evidence between 0.22 — 4.18°K . | 19 |
| Hf..... | Low purity..... | No evidence between 0.16 — 4.20°K . | 24 |
| Zr..... | 0.04 w/o Hf..... | 0.565°K —unannealed..... 0.546°K —annealed. | 18 |
| Zr..... | High purity..... | $0.70 \pm 0.02^\circ \text{K}$ | 17 |
| Ti..... | 99.95 w/o Ti..... | 0.588°K | 18 |

Thermoelectric Properties [2]

The thermoelectric properties of the platinum-hafnium couple in the temperature range 0 to 550°C are shown graphically in Figure

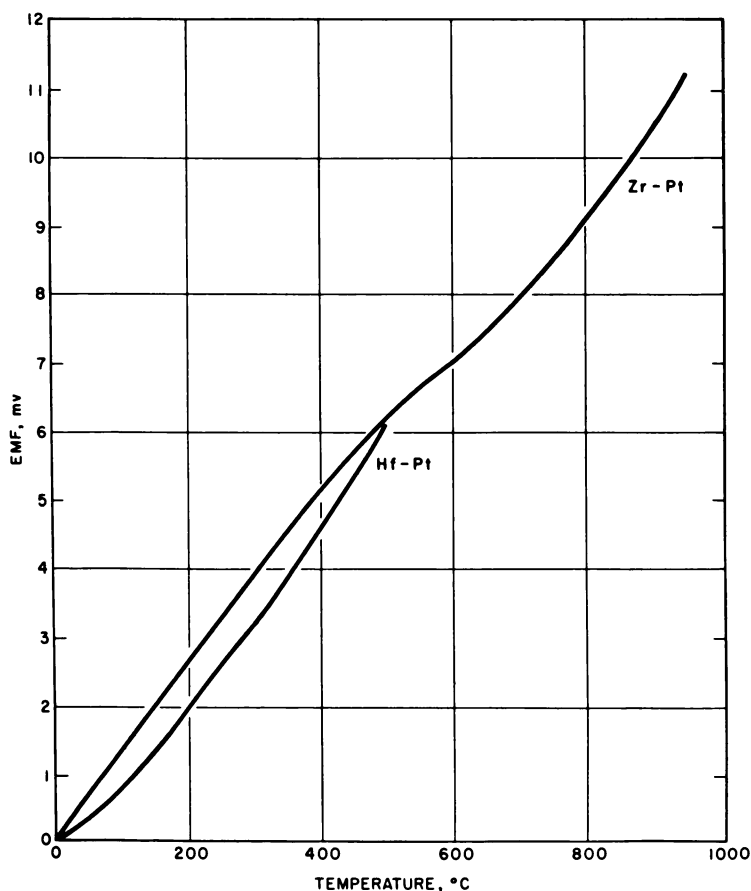


FIGURE 7.2. Thermoelectric Force of a Hafnium-Platinum Couple (Hf+; Pt-) Temperature Range 683 to 872°C : A, 872° ; B, 827° ; C, 803.5° ; D, 798.5° ; E, 779° ; (from Ref. 2 Courtesy of the American Society of Metals).

7.2, together with comparable data for the platinum-zirconium couple. The lack of more extensive data is undoubtedly accounted for by the fact that hafnium is unsuited for thermocouple use because of its propensity for occluding gases.

Linear Thermal Expansion

The coefficient of linear thermal expansion has been determined by several investigators [2, 23]. The data are summarized in Table 7.7 and Figure 7.3. Since hafnium has a hexagonal structure in the temperature range covered in these studies, it would be expected that the linear thermal expansion would be dependent upon the degree of preferred orientation existing in the material. This has not been amply accounted for in the work done thus far, so that the values given must be applied with caution. Comparison of the values for cold-worked material and annealed material suggests that thermal expansion in the [1010] direction is slightly less than the average (random) expansivity.

TABLE 7.7—COEFFICIENT OF LINEAR THERMAL EXPANSION
($10^{-6}/^{\circ}\text{C}$)

| Temperature ($^{\circ}\text{C}$) | Instantaneous | Average from 20°C to indicated temperature | Reference |
|------------------------------------|---------------|--|-----------|
| —183 | ----- | 5.4 (CW) ¹ | 2 |
| —183 | ----- | 5.7 (Ann) ² | 2 |
| —70 | ----- | 5.7 (CW) | 2 |
| —70 | ----- | 5.9 (Ann) | 2 |
| 100 | 6.8 | 6.6 | 23 |
| 200 | 6.3 | 6.7 | 23 |
| 204 | ----- | 5.9 (CW) | 2 |
| 300 | 5.8 | 6.3 | 23 |
| 316 | ----- | 5.9 | 2 |
| 316 | ----- | 6.2 (Ann) | 2 |
| 400 | 5.5 | 6.1 | 23 |
| 427 | ----- | 5.9 (CW) | 2 |
| 500 | 5.8 | 6.0 | 23 |
| 538 | ----- | 5.9 (CW) | 2 |
| 538 | ----- | 6.1 (Ann) | 2 |
| 600 | 5.5 | 5.9 | 23 |
| 649 | ----- | 5.7 (CW) | 2 |
| 700 | 5.5 | 6.1 | 23 |
| 760 | ----- | 5.7 (CW) | 2 |
| 760 | ----- | 6.0 (Ann) | 2 |
| 800 | 5.5 | 5.8 | 23 |
| 871 | ----- | 5.7 (CW) | 2 |
| 871 | ----- | 5.9 (Ann) | 2 |
| 900 | 5.5 | 5.9 | 23 |
| 952 | ----- | 5.7 (CW) | 2 |
| 1,000 | 5.5 | 5.5 | 23 |

(CW) ¹—cold swaged from iodide crystal bar, annealed at $1,000^{\circ}\text{C}$, cold swaged 20%.

(Ann) ²—cold swaged from iodide crystal bar, annealed at $1,000^{\circ}\text{C}$.

Purity: Material reported in Ref. 2 contained 0.86 w/o Zr (see sample B, Table 7.5). The purity of the material reported in Ref. 23 is unknown.

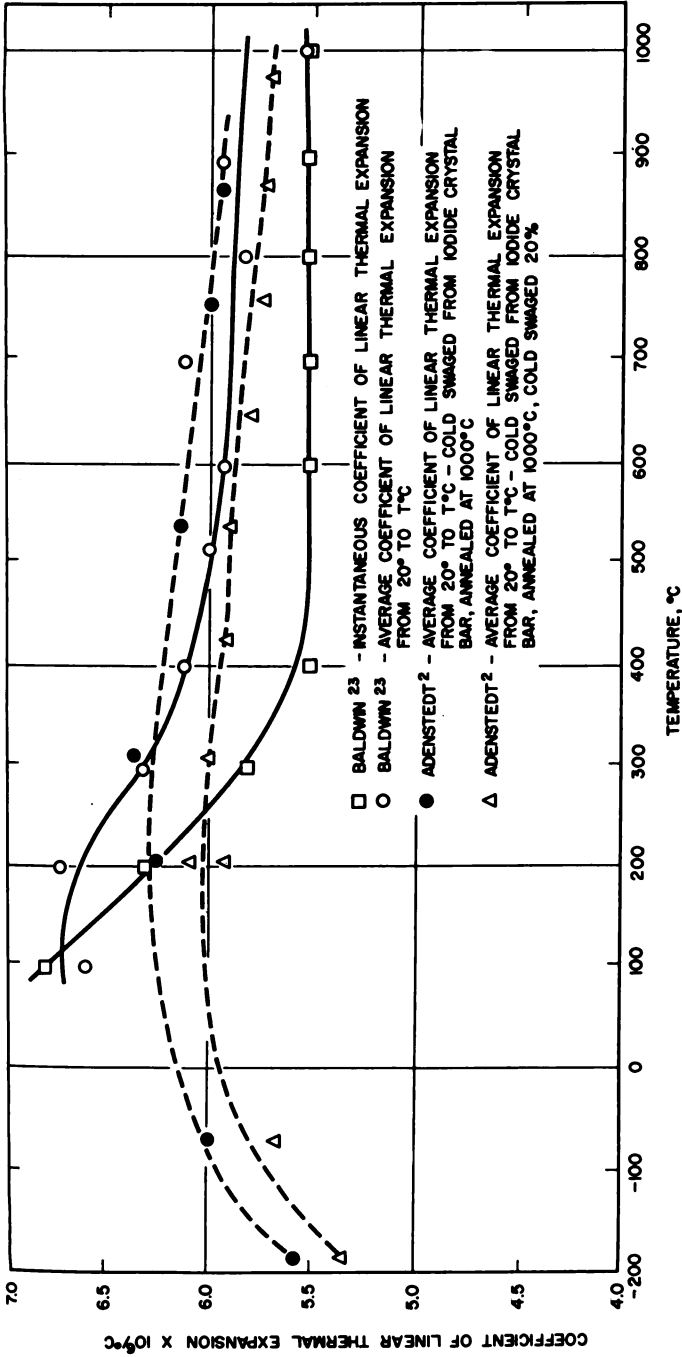


Figure 7.3. Coefficient of Linear Thermal Expansion vs. Temperature for Hafnium (from Ref. 2 Courtesy of the American Society of Metals).

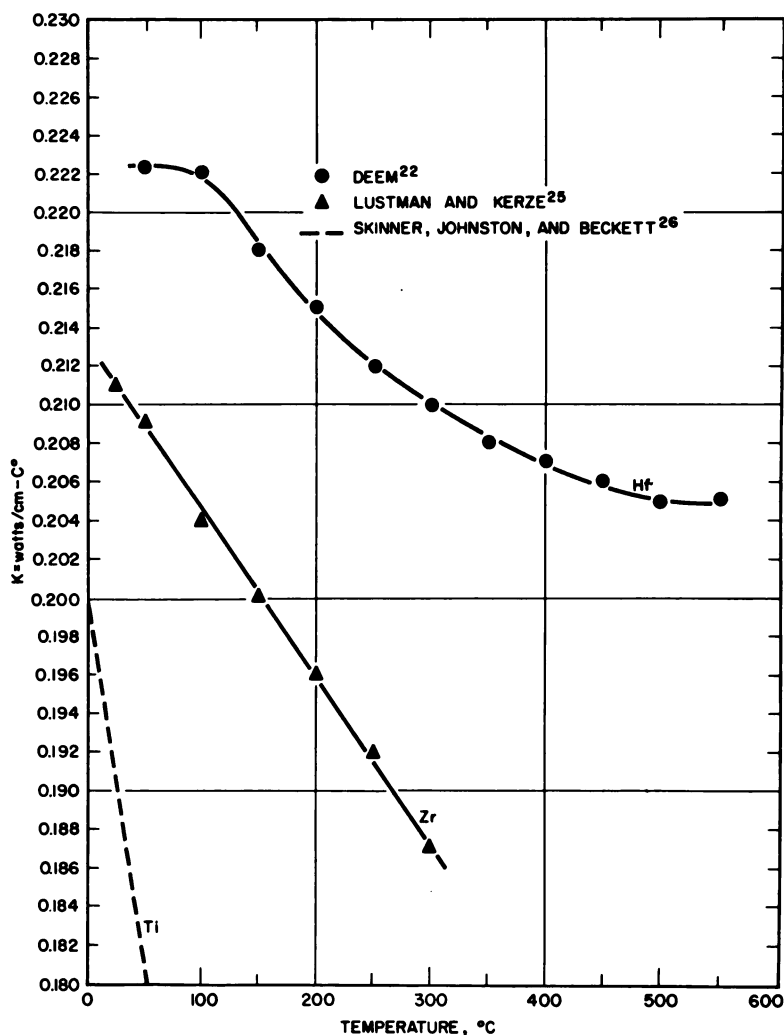


FIGURE 7.4. Thermal Conductivity of Hafnium, Zirconium, and Titanium between 50 and 550° C.

Thermal Conductivity

Deem [22] measured the thermal conductivity of hafnium containing 2 w/o zirconium between 50 and 550° C. The experimental results are shown graphically in Figure 7.4 and compared with those of zirconium [25] and titanium [26].

Density

The density values obtained for hafnium are summarized in Table 7.8. Much of the variation may be accounted for by differences in zirconium content and perhaps by variations of other impurities.

It has been found by investigators at Bettis Plant [27] that a 1 w/o variation in zirconium content brings about a 1 percent change in density.

TABLE 7.8—VALUES FOR DENSITY OF HAFNIUM

| Density (g/cc) | w/o Zirconium | Reference |
|--|-------------------|-----------|
| 13.19 | Sponge hafnium | 5 |
| 12.703 | Unknown | 16 |
| 13.36 (measured) | 0.78 ¹ | 4 |
| 13.90 (X-ray) | 0.78 | 4 |
| 13.20 | Unknown | 10 |
| 13.30 | Unknown | 1 |
| 13.011 ± 0.005 (measured) | 0.72 | 2 |
| 13.09 ± 0.01 (preferred value) (corrected for 1.4 a/o Zr). | 0.72 | 2 |

¹ Table 7.5, sample A.

Magnetic Susceptibility

The paramagnetic susceptibility for hafnium, which has been measured from 4.2 to 1,670° K [28], increases with increasing temperature. The room-temperature value is $(0.42 \pm 0.01) \times 10^{-6}$ emu/g. The curve of paramagnetic susceptibility versus temperature is given in Figure 7.5.

Hall Effect

The Hall constants for hafnium and zirconium were determined by Foner [29] to be -0.162×10^{-13} v cm/amp gauss for hafnium and $+12.6 \times 10^{-13}$ v cm/amp gauss for zirconium as compared with a value of $+0.95 \times 10^{-13}$ v cm/amp gauss for titanium.

Foner, in his discussion, presents two possible models which could explain the observed Hall effect. The models are based on the as-

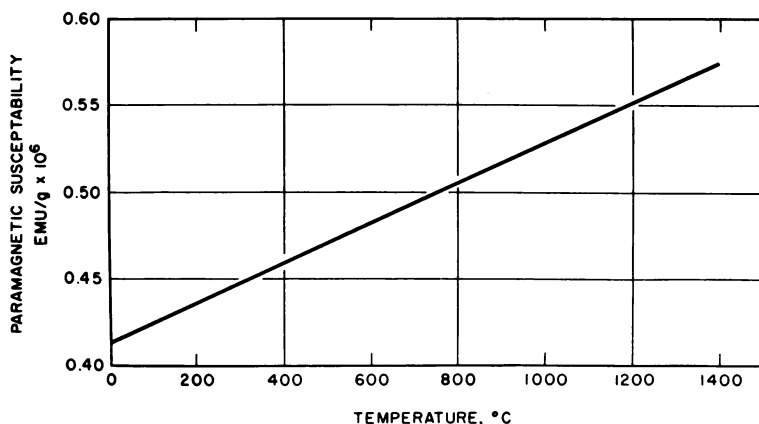


FIGURE 7.5. Paramagnetic Susceptibility of Hafnium vs. Temperature between 0 and 1400° C; Kriessmann and McGuire [28].

sumption that, for zirconium and hafnium respectively, the 5s and 4d or 6s and 5d bands are similar to the 4s and 3d bands in the iron group of transition elements.

If the Fermi level occurs near the top of the appropriate s and p bands, the positive Hall effect may be due to hole conduction in these bands. Secondly, if the appropriate s and p bands are nearly empty, and a positive Hall effect is observed, one assumes that there is no appreciable overlap of the (s, p) and d bands, i.e., the bottom of the (s, p) band is above the Fermi level. This may explain the positive Hall effect and the conductivity attributed to d-band holes.

In the second model, for titanium and hafnium, there appears to be a slight overlap of the appropriate s and d bands so that the Hall constant is very small. The sensitivity of the Hall coefficient to small amounts of impurities could be explained on the basis of either a small change in overlap of the appropriate s and d bands, or possibly by the introduction of impurity level bands.

Electron Emission

The electron emission characteristics of hafnium and zirconium are compared in Table 7.9.

TABLE 7.9—ELECTRON EMISSION DATA FOR HAFNIUM AND ZIRCONIUM

| <i>T</i> (°K) | <i>Electron emission (milliamp/cm²)</i> | |
|---------------|--|-----------------------|
| | <i>Hafnium</i> [30] | <i>Zirconium</i> [31] |
| 1, 900----- | 4. 80 | 40. 5 |
| 2, 000----- | 26. 2 | 160 |
| 2, 100----- | 123 | 520 |
| 2, 200----- | 485 | 720 |

Since no data on the emissivity of hafnium had been reported at the time, Zwicker [30] estimated a value of 0.37 in order to correct his pyrometer readings to true temperatures. A temperature error of about 50° would be expected from the uncertainty in the emissivity value.

Total Emissivity

Unpublished data of J. Huminick on the total emissivity of hafnium as a function of temperature are presented in Table 7.10.

TABLE 7.10—TOTAL EMISSIVITY

| <i>Black body temperature</i> (°C) | <i>Emissivity</i> |
|------------------------------------|-------------------|
| 266----- | 0. 52 |
| 364----- | 0. 52 |
| 535----- | 0. 56 |
| 540----- | 0. 56 |
| 544----- | 0. 56 |
| 550----- | 0. 56 |

Compressibility

Bridgeman [21] measured the compressibility of hafnium at 30 and 75° C and obtained the following equations which are valid up to pressures of approximately 12,000 kg/cm²:

$$30^{\circ} \text{ C: } \frac{\Delta V}{V} = 9.01 \times 10^{-7} p = 2.37 \times 10^{-12} p^2$$

$$75^{\circ} \text{ C: } \frac{\Delta V}{V} = 8.81 \times 10^{-7} p = 2.37 \times 10^{-12} p^2$$

where V = volume (cc)

p = pressure (kg/cm²)

Specific Heat

Cristescu and Simon [32] measured specific heat from 13 to 210° K and found a maximum at approximately 75° K. However, it is believed that their sample was mostly HfO₂ [33]. Burke and Darnell [34], and Friedberg [35] found no maximum in the specific heat curve in the same temperature range for samples containing 2 w/o zirconium. The curves for specific heat measured over the range of 15 to 200° K by Friedberg [35] are plotted in Figure 7.6. Specific heat data for the range of 2 to 20° K, obtained by Wolcott [33], are plotted in Figure 7.7. Data obtained on the Debye Temperature by both Friedberg and Wolcott have been combined in Figure 7.8.

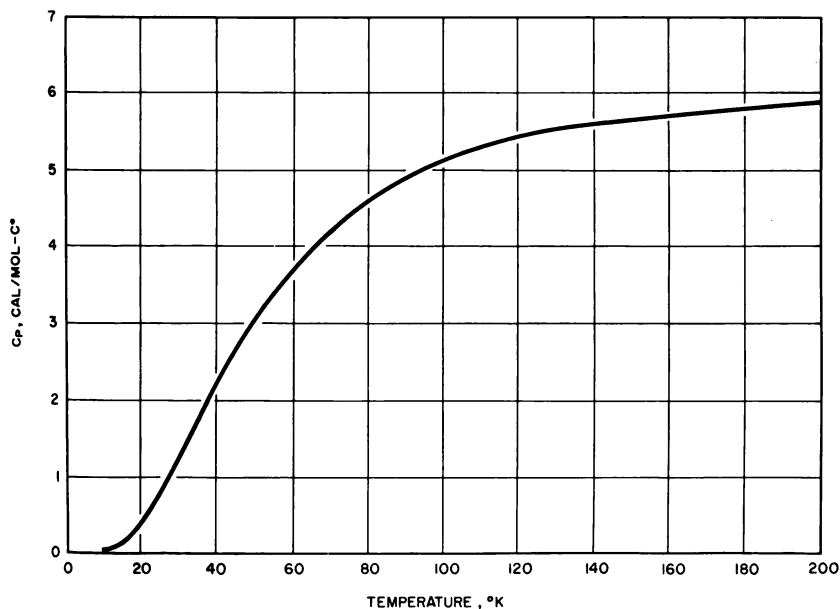


FIGURE 7.6. Specific Heat of Hafnium vs. Temperature between 15 and 200° K; Friedberg [35].

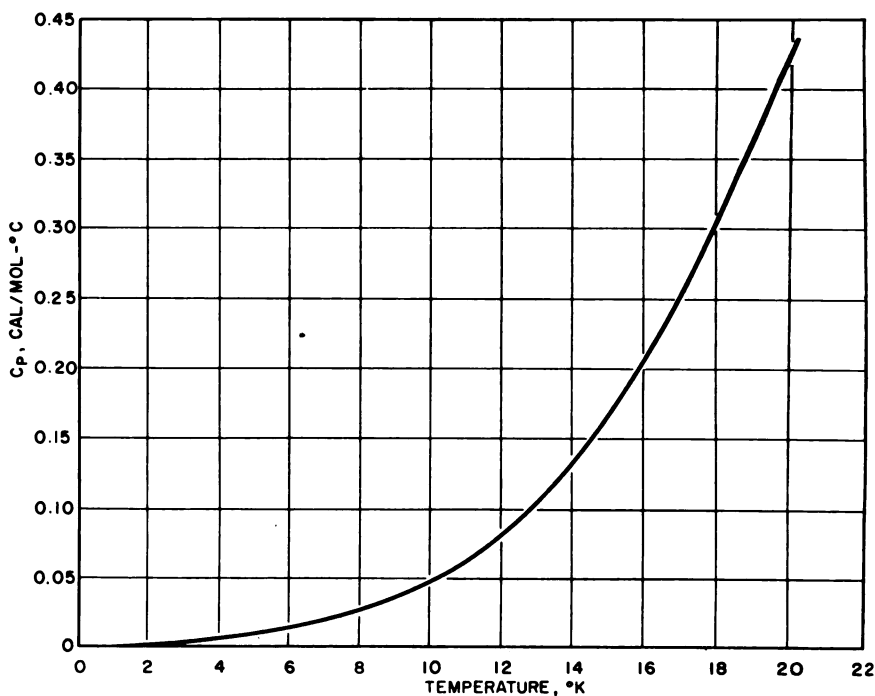


FIGURE 7.7. Specific Heat of Hafnium vs. Temperature between 2 and 20° K; Wolcott [33].

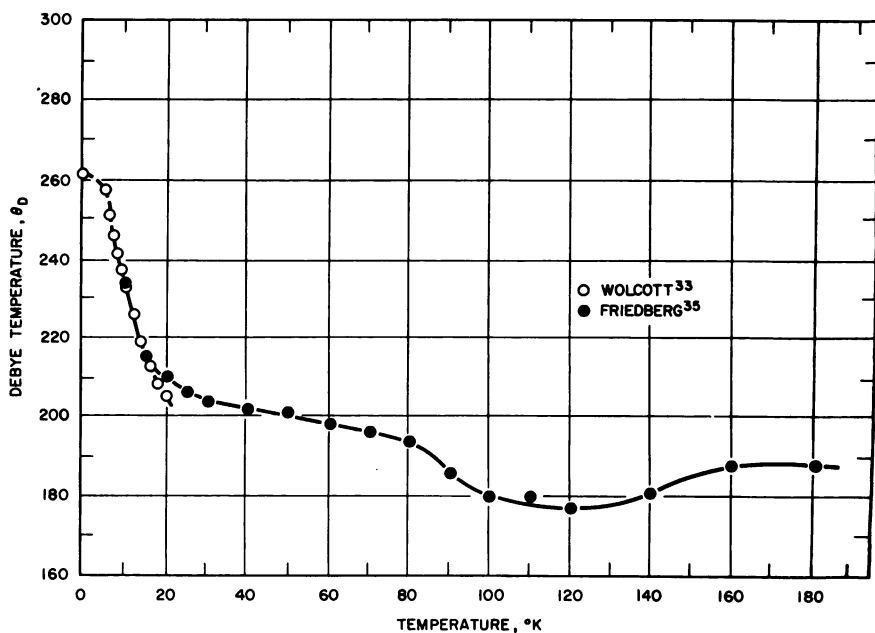


FIGURE 7.8. Debye Temperature (θ_D) of Hafnium vs. Temperature between 0 and 180° K; Combined Data of Friedberg [35] and Wolcott [33].

Adenstedt [2] reported a value for C_p of 6.24 cal/mol-°C between 25 and 100° C.

Stull and Sinke [36] estimated the specific heat, C_p , from room temperature to the melting temperature. They used the value of 1,975° C reported by Adenstedt for the melting point of hafnium and neglected the allotropic transformation from close-packed hexagonal to body-centered cubic. All heat effects associated with the alpha-beta transformation and the solid to liquid transformation were included in their estimate of the heat of fusion which was used to calculate the C_p value for the liquid. Their estimate of C_p is based on the measured values between 50 and 200° K reported by Friedberg [35] and shown in Figure 7.6. The values for C_p estimated by Stull and Sinke are tabulated in Table 7.11.

TABLE 7.11—SPECIFIC HEAT, C_p , VS. TEMPERATURE ESTIMATED BY STULL AND SINKE [36]

| $T(^{\circ}\text{K})$ | $C_p(\text{cal/mol-}^{\circ}\text{C})$ | $T(^{\circ}\text{K})$ | $C_p(\text{cal/mol-}^{\circ}\text{C})$ |
|-----------------------|--|-----------------------|--|
| 300..... | 6. 10 | 1, 400..... | 7. 42 |
| 400..... | 6. 22 | 1, 500..... | 7. 54 |
| 500..... | 6. 34 | 1, 600..... | 7. 66 |
| 600..... | 6. 46 | 1, 700..... | 7. 78 |
| 700..... | 6. 58 | 1, 800..... | 7. 90 |
| 800..... | 6. 70 | 1, 900..... | 8. 02 |
| 900..... | 6. 82 | 2, 000..... | 8. 14 |
| 1, 000..... | 6. 94 | 2, 100..... | 8. 26 |
| 1, 100..... | 7. 06 | 2, 200..... | 8. 38 |
| 1, 200..... | 7. 18 | 2, 300-3, 000..... | 8. 00 |
| 1, 300..... | 7. 30 | | |

Note: Reference state—solid from 298 to 2250° K; liquid from 2250 to 3000° K

Atomic Properties [37, 38]

The element hafnium has an atomic number of 72, an atomic weight on the physical scale of 178.50, and an atomic weight on the chemical scale of 178.543. The stable isotopes of hafnium and their abundance are given in Table 1.3 (Chap. 1). The atomic number of hafnium requires that it be placed in Group IV and period 6 of the periodic table, whence its characteristic valence should be 4 and maximum coordination number 8. The other members of Group IV-A are titanium, zirconium, and thorium.

The chemical properties of these elements are similar, and the remarkable similarity between the elements zirconium and hafnium can be partially explained by the perfectly similar arrangements of electrons in their two outermost quantum levels and their nearly identical atomic size.

The electron configurations of zirconium and hafnium are:

Zr $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^2 5s^2$

Hf $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^2 6s^2$

The expansion of hafnium over zirconium in going from the fifth to the sixth period is compensated for by the contraction in filling the fourth quantum group (lanthanide contraction) which occurs in the elements from atomic number 58 to atomic number 71. The atomic radius, ionic radius, and atomic volume for hafnium and zirconium are shown below:

| <i>Element</i> | <i>Atomic radius (Å)</i> | <i>Atomic volume ¹ (Å)</i> | <i>Ionic radius (Å)</i> |
|----------------|------------------------------|---|-----------------------------|
| Hafnium----- | 1.442 | 13.42 | 0.75 |
| Zirconium----- | 1.452 | 13.97 | 0.74 |

¹ From Ref. 3.

Other elements such as silver and gold have similar electronic configurations and close atomic size, but their chemical properties are not too similar. The above explanation, therefore, is not sufficient to explain the almost perfect similarity in chemical properties between hafnium and zirconium. This suggests that the field effect of the underlying quantum levels of electrons on the valency electrons is nearly identical.

The first ionization potential of hafnium is 7.3 ev. The standard potential for hafnium ions in aqueous solution is 1.57 volts compared with 1.43 volts for zirconium.

7.3 MECHANICAL PROPERTIES OF HAFNIUM

By W. B. Haynes,² J. G. Weinberg,² W. D. McMullen,² and R. E. Johnson²

The mechanical properties of hafnium have been determined by several investigators. They include transverse and longitudinal tensile properties at room and elevated temperatures, hardness, impact properties over a range of temperatures, creep properties, and fatigue properties. Where available, information is presented showing the effect of impurities and thermal history on these properties. To allow for an evaluation of hafnium as an engineering material, its fatigue and creep properties are compared with those of the more common engineering materials.

Tensile Properties

The tensile properties to be presented here refer exclusively to those of strip produced from arc melted iodide crystal bar. Because these properties are influenced to a great degree by the thermal his-

² Westinghouse Atomic Power Division.

tory of the material, as well as by the impurity content, the data obtained by the several investigators exhibit a fair degree of scatter. To present a reasonably clear picture of the tensile properties of hafnium, those obtained on fully-annealed material are presented first. Typical properties of material annealed at somewhat lower temperatures are then shown for comparison. The effect of cold work and copper content on tensile properties is also demonstrated.

The tensile properties [40, 41] of material annealed at 926°C ($1,700^{\circ}\text{F}$) for 15 minutes are presented in Table 7.12 and in Figure 7.9. Both yield and tensile strength show a steady regular decline with temperatures from 80 to 700°F . That a slight anisotropy in tensile properties exists is shown by the difference between longitudinal and transverse properties at 80 and 700°F . Transverse tensile strength at 80 and 700°F is lower than the longitudinal value. Transverse yield strength at these same two temperatures is, however, higher than the corresponding longitudinal values. Similar behavior is seen in zirconium.

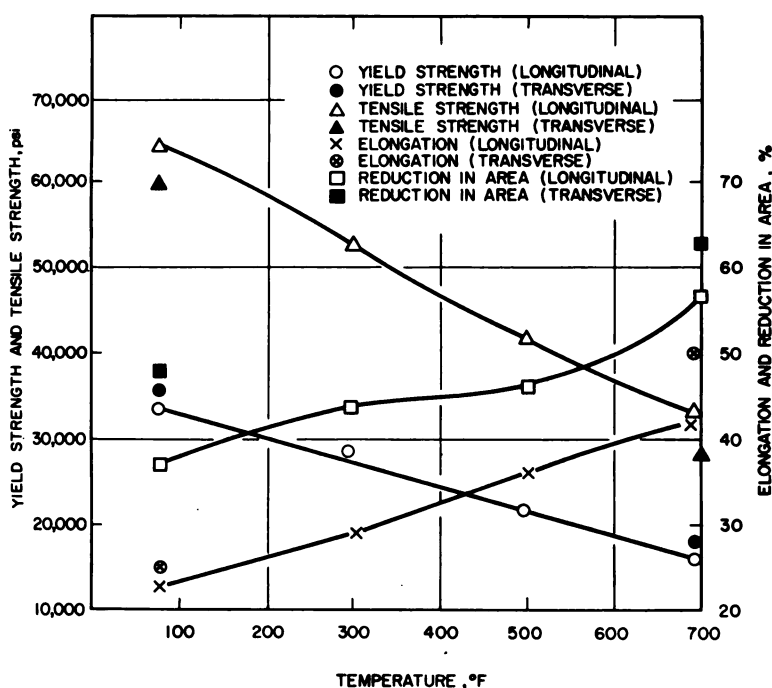


FIGURE 7.9. Tensile Properties as a Function of Temperature; Arc-Melted Iodide Hafnium, Annealed at 926°C ($1,700^{\circ}\text{F}$) for 15 Minutes.

TABLE 7.12—TYPICAL MECHANICAL PROPERTIES OF ANNEALED ARC MELTED IODIDE HAFNIUM STRIP

A. AVERAGE LONGITUDINAL TENSILE PROPERTIES OF ANNEALED STRIP ¹

| Temperature | | 0.2% yield strength (psi) | | Ultimate tensile strength (psi) | | Elongation (%) | | Percent reduction in area | |
|-------------|-----|---------------------------|-----------|---------------------------------|-----------|----------------|-----------|---------------------------|-----------|
| ° C | ° F | Ave. | Std. Dev. | Ave. | Std. Dev. | Ave. | Std. Dev. | Ave. | Std. Dev. |
| 27 | 80 | 33,600 | 3,100 | 64,800 | 5,300 | 23 | 3.5 | 37 | 2.5 |
| 149 | 300 | 28,700 | 2,400 | 53,200 | 4,100 | 29 | 4.6 | 44 | 3.6 |
| 260 | 500 | 22,300 | 2,250 | 42,000 | 3,200 | 36 | 6.1 | 46 | 3.9 |
| 371 | 700 | 15,700 | 1,300 | 33,700 | 2,100 | 43 | 8.6 | 57 | 3.7 |

B. AVERAGE TRANSVERSE TENSILE PROPERTIES OF ANNEALED STRIP ¹

| | | | | | | | | | |
|-----|-----|--------|-------|--------|-------|----|-----|----|-----|
| 27 | 80 | 39,600 | 3,200 | 60,100 | 3,600 | 25 | 5.8 | 38 | 4.4 |
| 371 | 700 | 18,100 | 1,300 | 28,600 | 1,700 | 50 | 9.2 | 63 | 5.5 |

C. EFFECT OF 15% COLD REDUCTION ON LONGITUDINAL TENSILE PROPERTIES ²

| Temperature | | 0.2% yield strength (psi) | Ultimate tensile strength (psi) |
|-------------|-----|---------------------------|---------------------------------|
| ° C | ° F | | |
| 27 | 80 | 50,000 | 79,000 |
| 260 | 500 | 35,000 | 50,000 |

¹ Annealed for 15 min at 926° C (1,700° F).² Cold rolling followed by 1-hr anneal at 704° C (1,300° F).

Tensile properties for hafnium heat treated at 750° C (1,382° F) for 30 minutes are plotted in Figure 7.10 [42–45].

If the values in Figure 7.10 are compared with those in Figure 7.9, it is seen that the variation of properties with temperature is essentially the same. The difference appears to be in the amount of scatter in the average values. The results of Figure 7.9 are based on material annealed at 926° C for 15 minutes, whereas those of Figure 7.10 refer to material annealed at a lower temperature, 750° C, for 30 minutes. Data presented in the physical metallurgy section indicate that the material is not fully annealed until it is heated to at least 900° C. Therefore, more scatter is to be expected in the properties of the material treated at 750° C than in those of the material annealed at 926° C.

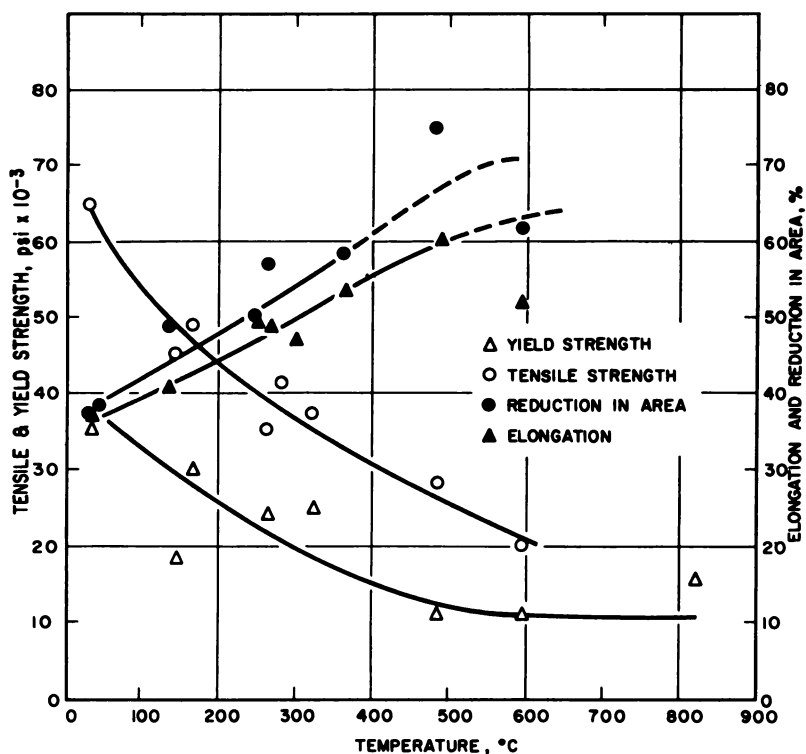


FIGURE 7.10. Tensile Properties as a Function of Temperature; Arc-Melted Iodide Hafnium, Heat Treated at 750° C (1382° F).

Some interesting observations on the mode of fracture of hafnium tensile specimens have been made by Johnson [46]. Johnson used vacuum-melted iodide hafnium which was hot rolled to strip, heat treated in vacuum for one hour at 700° C, and furnace cooled. The tensile data, obtained over a range of temperatures of 25 to 800° C, are shown in Figure 7.11. These data compare favorably with those shown in Figures 7.9 and 7.10. There are several points about these data that should be emphasized.

1. *Apparent upper yield point*—Several load-elongation curves showed a maximum load value at an elongation smaller than that associated with necking down. This was observed only when testing transverse specimens and was most pronounced at 200° C. Two load-elongation curves, shown in Figure 7.12, illustrate this point. The load-elongation curve for a transverse specimen tested at 200° C and showing this effect is shown along with one tested at 600° C in which the effect is not quite so pronounced. Johnson interprets this phenomenon as being associated with grain boundary rotation during testing whereby a reduction in load may occur as particular slip

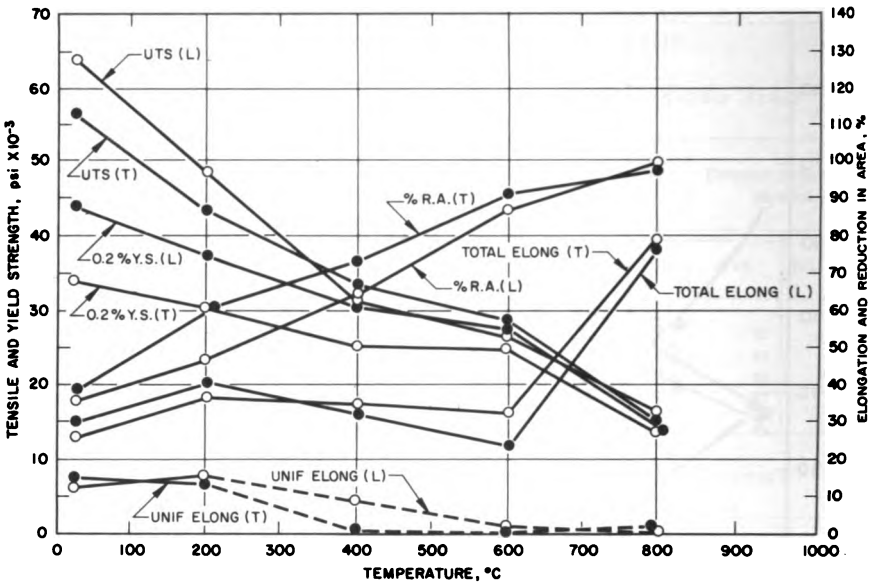


FIGURE 7.11. Tensile Properties as a Function of Temperature; Vacuum Arc-Melted Hafnium, Heated 1 Hour at 700°C (1292°F); Strain Rate 5 Percent per Minute.

systems become aligned in the direction of the critical resolved shear stress. If this is, in fact, the mechanism, then it would be expected that the appearance of the observed phenomenon should be sensitive to specimen orientation. The fact that this phenomenon has been observed only for transverse specimens tends to confirm these views. Furthermore, this observed behavior, according to the proposed mechanism, should also be temperature dependent, because, as the temperature increases, it is easier for grains to rotate, and thus more active slip systems become available. The fact that the appearance of the yield point is more pronounced at 200°C than it is at 600°C again confirms the proposed mechanism.

2. *Uniform elongation*—In Figure 7.11, the uncertainty of the uniform elongation at the higher temperature arises from an interpretation of the load-elongation curve. As noted in Figure 7.11, at temperatures in the vicinity of 400°C , the curve for the longitudinal specimens reaches a maximum and then continuously decreases. In many materials which exhibit considerable work hardening tendencies, the maximum in the load-elongation curve has been found to correlate quite well with the point of mechanical instability. There is no assurance, however, in the case of hafnium, that necking down at high temperatures actually begins at strains slightly in excess of the 0.2 percent offset yield strength. If, in fact, a mechanism such as grain rotation does bring about a reduction of load under exten-

sion, the maximum in the load-elongation curve would not be an adequate measure of the usually accepted meaning of uniform elongation. Unfortunately, the actual strain at which mechanical instability did occur in the various specimens was not determined.

3. *Reduction of area*—Measurement of the reduction of area of these specimens was relatively complex for, as temperature of testing increased, the fracture area became more and more elliptical. These are shown in Figure 7.13.

Johnson further interprets his tensile property data in terms of the possible existence of a strain-hardening phenomenon at temperature near 500°C extending over a 400°C range of temperatures. This behavior is reflected especially by transverse total elongation data but not particularly by the data on reduction in area. This kind of behavior has been noted previously in zirconium and Zircaloy-2 by Mehan [47].

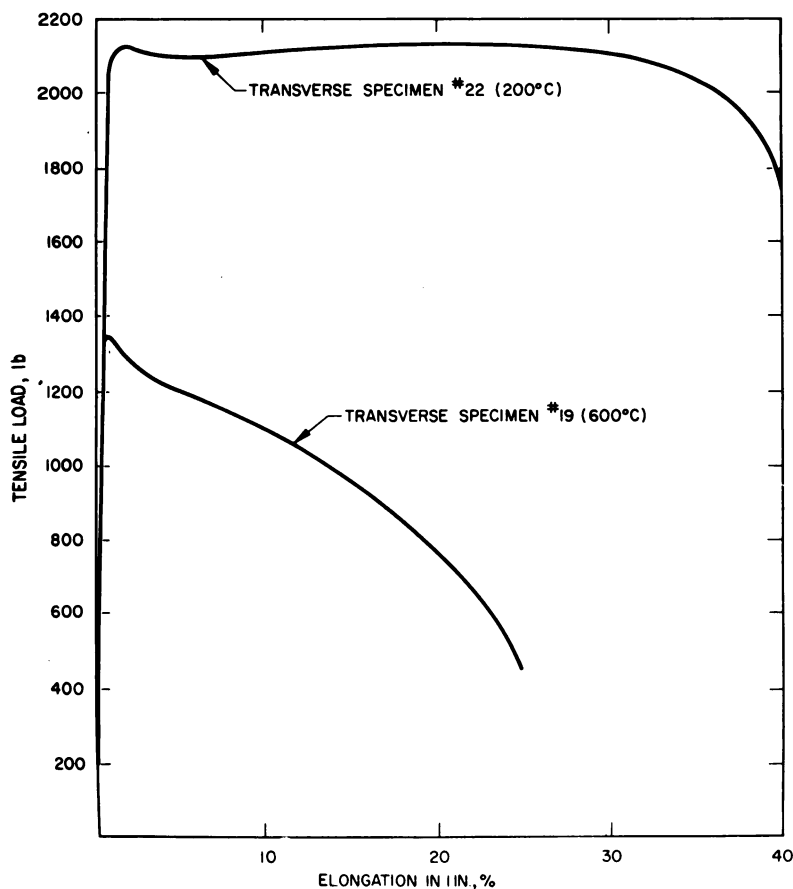


FIGURE 7.12. Load Elongation Curves for Transverse Specimens of Hot-Rolled Vacuum-Melted Iodine Hafnium Tested at the Indicated Temperatures; the Top Curve Displays an Apparent Upper Yield Point.

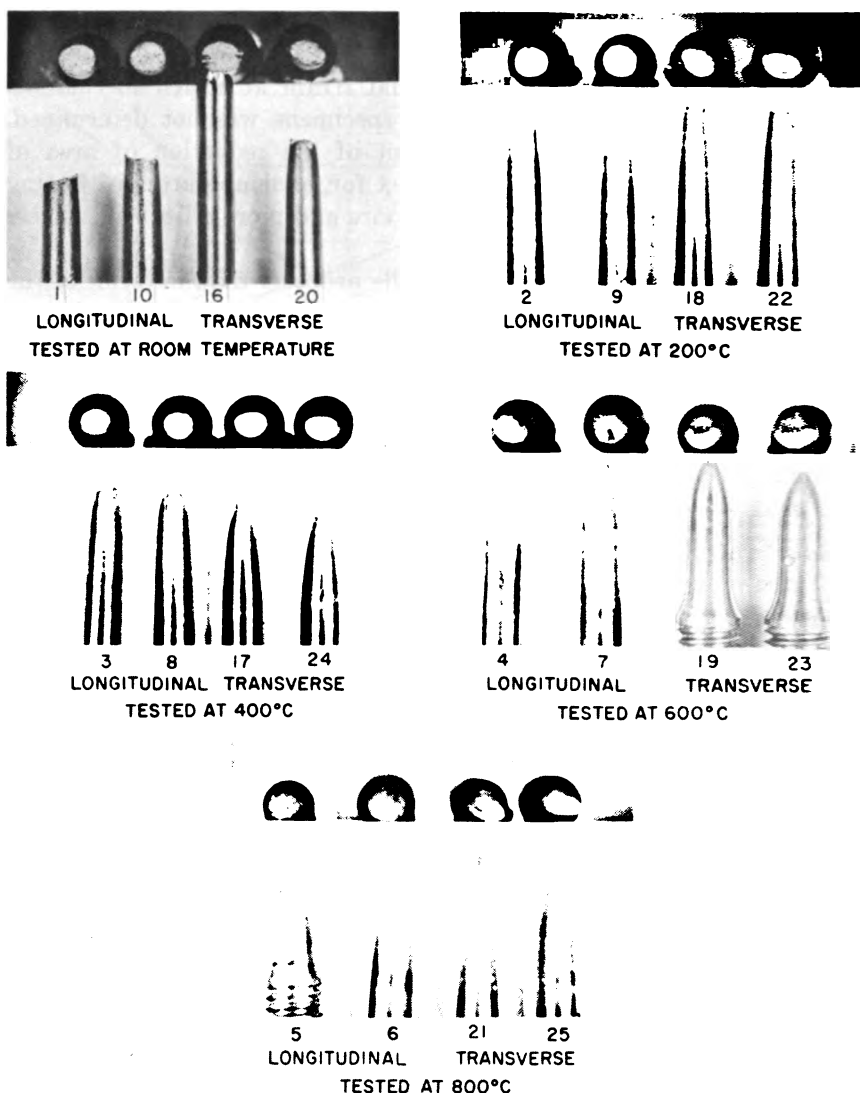


FIGURE 7.13. Vacuum-Melted Hafnium Crystal-Bar Tensile Specimens; Orientations, Specimen Numbers, and Testing Temperatures Are as Indicated.

No firm explanation is available for the observed "yield point" behavior in the load-elongation curves of some of the transverse specimens or for the triangular-shaped fractures of the longitudinal specimens.

True Stress-Natural Strain Curves

Figure 7.14 shows true stress-natural strain curves plotted for high purity iodide hafnium, titanium, and zirconium. The curve for

hafnium refers to the vacuum-melted material discussed in the previous section [46]. The curve for zirconium represents high purity crystal bar zirconium sheet samples (longitudinal) annealed in vacuum for 20 hours at 750° C and furnace cooled [31]. The curve for titanium relates to high purity crystal bar titanium [48], arc melted, hot rolled, annealed to obtain 0.01 mm minimum grain size, and tested at a cross-head speed of 0.005 in./min. until plastic strains were attained. At this point, the cross-head speed was changed to 0.01 in./min. A 1/8-inch diameter, round, longitudinal specimen was used.

Generally, these three high purity materials exhibit true stress-natural strain curves which appear to be related to the c/a ratio of each of these close-packed hexagonal metals. It is interesting to note that the c/a ratios of these three metals, shown in Table 7.13, are less than the ideal ratio for closest atomic packing (1.633). Furthermore, inspection of the curves in Figure 7.14 indicates that, with respect to increasing strength and increasing rate of work hardening as indicated by the slope of the linear portion of the plastic region, the order of the metals is zirconium, titanium, and hafnium. Comparison of this information with that in Table 7.13 indicates that the order of increasing deviation from the ideal c/a ratio is the same as that for increasing strength and increasing rate of work hardening. Thus, it is evident that for the hexagonal metals, hafnium, zirconium, and titanium, the c/a ratio is at least a qualitative indication of the nature of the true stress-natural strain curve.

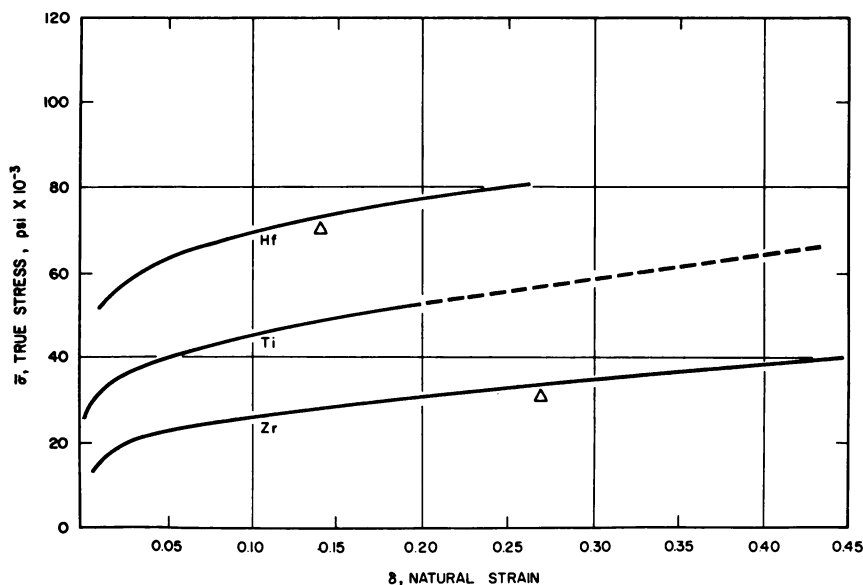


FIGURE 7.14. True Stress Natural Strain Curve for High Purity Iodide Hafnium, Zirconium, and Titanium.

This behavior is probably related to the allowable degree of lattice slip as the ideal c/a ratio is approached.

When true stress-natural strain data for hafnium, zirconium, and titanium are plotted logarithmically ($\log_e \bar{\sigma}$ vs $\log_e \delta$), a straight line relationship exists in the plastic region up to and perhaps just beyond the limit of uniform tensile strain. The empirical relation $\bar{\sigma} = K \delta^n$ can therefore be applied. The coefficient, n , which is a measure of the capacity of the material to work harden, is the slope of the logarithmic curve described above. Table 7.14 shows some values of n for hafnium, titanium, and zirconium.

TABLE 7.13— c/a RATIOS FOR HAFNIUM, ZIRCONIUM, AND TITANIUM

| <i>Metal</i> | <i>c/a Ratio</i> |
|----------------|------------------|
| Zirconium..... | 1.593 |
| Titanium..... | 1.587 |
| Hafnium..... | 1.581 |

TABLE 7.14—WORK HARDENING COEFFICIENTS FOR HAFNIUM, TITANIUM, AND ZIRCONIUM

| <i>Metal</i> | <i>n</i> | <i>Reference</i> |
|----------------|----------------|------------------|
| Hafnium..... | 0.14..... | 46 |
| Titanium..... | 0.09–0.16..... | 31 |
| Zirconium..... | 0.05–0.25..... | 31 |

Because the actual value of n depends to a significant extent on the degree of prior cold work in a material, nothing more can be said about the value for hafnium other than that it is within the range of values exhibited by titanium and zirconium.

The Effect of Copper on Tensile Properties [43, 45]

Figure 7.15 shows the manner in which copper increases yield strength and decreases total elongation for hafnium strip tested in the longitudinal direction. Again, this material was not fully annealed so that a considerable scatter appears, particularly in the yield strength values. It appears that an impurity level of 60 ppm of copper increases the yield strength about 15 to 20 percent above that for a copper level of approximately 10 ppm. The significance of this effect of copper on hardness is that increasing copper above 120 ppm leads to a loss of fabricability.

Hardness

The hardness of hafnium is influenced very markedly by the amount of cold reduction the material has received [42]. Figure 7.16, which is a plot of hardness versus cold reduction, indicates that

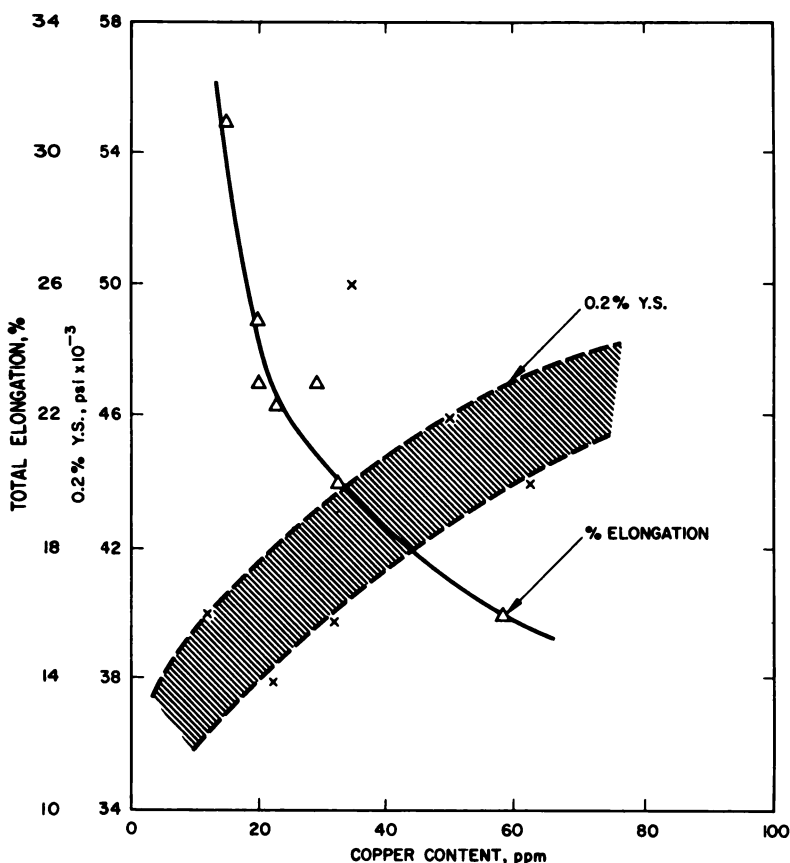


FIGURE 7.15. Yield Strength and Percent Elongation as a Function of Copper Content for Arc-Melted Iodide Hafnium Strip; Longitudinal Orientation, Heated at 750° C for 1 Hour.

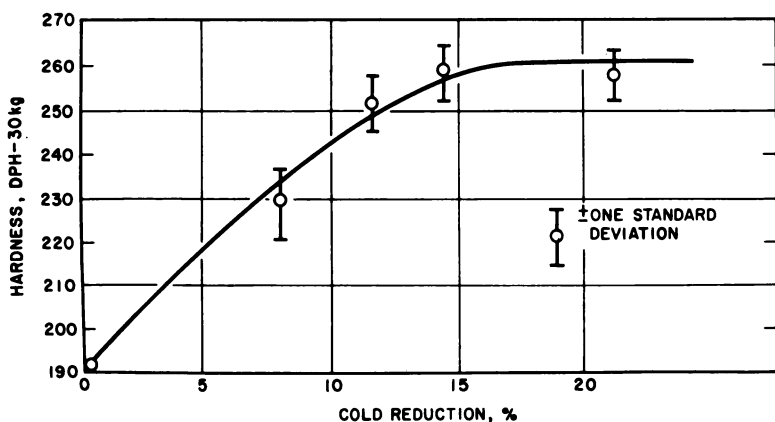


FIGURE 7.16. Hardness vs. Percent Reduction in Cold Rolling; Arc-Melted Iodide Hafnium.

up to about 12 percent cold reduction by rolling, the hardness increases linearly from 190 at zero percent to about 260 DPH. Above 12 percent cold reduction, the hardness values appear to approach a level of approximately 265 DPH. This significant effect of cold work on hardness is very likely reflected in strength values and points up the importance of annealing at a temperature high enough to remove all traces of cold work to obtain consistent and reproducible tensile results.

Impact Properties

The impact properties of annealed, arc melted crystal bar hafnium have been determined in a combined study by Wessel [40] and Goodwin and Lorenz [41]. Longitudinal subsize Izod specimens, 0.2 x 0.2 x 1.5 inches, with "V" notches machined perpendicular to the rolling plane were cut from hot rolled strip which had been annealed at 926° C (1,700° F) for 15 minutes. Samples were then tested over a range of temperatures from -100 to 600° F on a Bell Telephone Laboratory Impact Machine. Selected data from these studies are tabulated in Table 7.15 and are plotted in Figure 7.17. Several features of these data are worthy of mention: (1) the amount of energy absorbed at each temperature is relatively low; (2) at 93° C (200° F) and higher, the specimens did not fracture completely. The

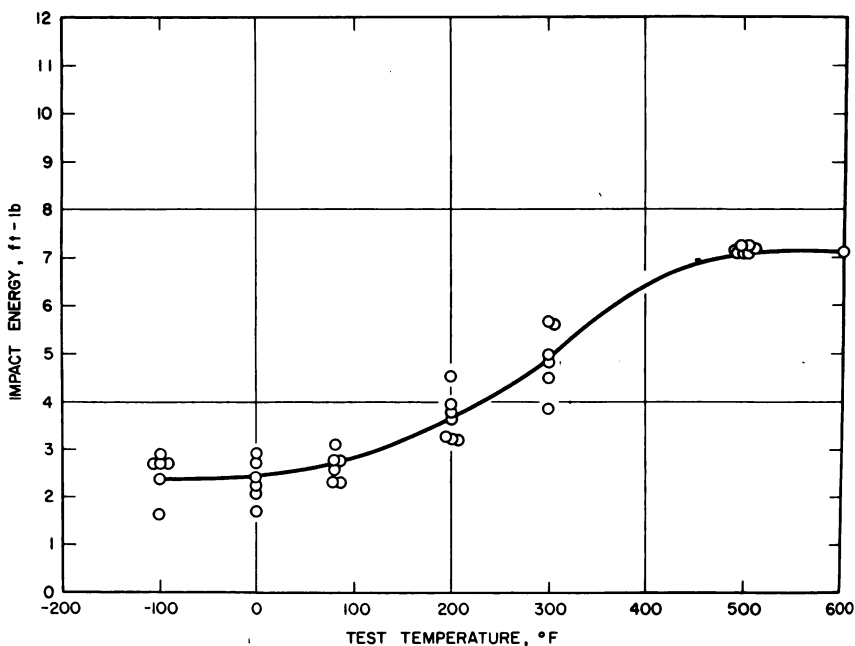


FIGURE 7.17. Average Impact Properties of Arc-Melted Iodide Hafnium Strip, Transverse Specimens; Annealed at 1,700° F for 15 Minutes.

magnitude of the values reflects the fact that subsize samples were used. The fact that specimens above 93° C (200° F) did not fracture completely detracts from the meaning of the values of energy absorbed for each of these specimens. Zircaloy-2 subsize impact specimens also exhibit both low impact strength values and incomplete fracture.

It is difficult to interpret such data in terms of describing hafnium as a brittle or a ductile material. These data do not indicate clearly a transition temperature. Although Wessel suggests that the appearance of the fracture at temperatures below 93° C (200° F) indicates a brittle condition, recent unpublished results obtained at Bettis indicate subsize impact specimens of comparable material fracture in a ductile manner as revealed by careful measurements of the fracture area. Lack of more extensive data on this subject precludes any further discussion at this time.

TABLE 7.15—IMPACT DATA ON ANNEALED, ARC MELTED, CRYSTAL BAR HAFNIUM

| Test temperature | | Energy absorbed (ft-lb) | Remarks |
|------------------|------|-------------------------|---|
| °C | °F | | |
| —73 | —100 | 1.6 to 2.8----- | Total failure. |
| —18 | 0 | 1.7 to 3.0----- | Total failure. |
| 27 | 80 | 2.3 to 3.1----- | Total failure. |
| 93 | 200 | 3.2 to 4.5----- | Incomplete failure (90% of cross section failed). |
| 149 | 300 | 3.9 to 5.8----- | Incomplete failure (80%–90% of cross section failed). |
| 260 | 500 | 7.1----- | Incomplete failure (50% of cross section failed). |
| 316 | 600 | 7.0----- | Incomplete failure (50% of cross section failed). |

The Effect of Irradiation on the Properties of Hafnium

Very little work has been done on this subject. The data that do exist are quite sparse and incomplete. Goodwin and Lorenz [41] performed pre-post studies on the effect of neutron irradiation on the impact strength and hardness of arc melted crystal bar hafnium. Irradiations were performed on specimens in NaK-filled capsules whose temperatures were neither controlled nor measured. The total integrated neutron flux varied from 3 to 9×10^{20} nvt in which the ratio of thermal to fast flux was estimated to be 20:1. Room temperature impact values of the irradiated subsize Izod impact specimens are approximately 60 percent of those of the unirradiated specimens.

Furthermore, the average hardness value of the irradiated specimens (245 DPH) is approximately 35 percent higher than that of the unirradiated specimens (179 DPH). Although these qualitative trends are evident, no further interpretation of these data should be made.

Very recent unpublished results have been obtained at Bettis Plant on the effect of neutron irradiation on the properties at room temperature, 149° C (300° F), and 371° C (700° F) of arc-melted crystal bar hafnium exposed to an integrated fast flux of 2×10^{21} nvt (>1 mev) at a temperature of 245° C (470° F). These data are shown in Table 7.16. These results are to be compared with typical values of material with comparable thermal history, Figure 7.10. Such a comparison indicates that a significant (factor of two) increase in yield strength has been brought about in the irradiated samples. It is interesting to note that the tensile strength has increased only slightly, and the ductility, except for the elongation at 371° C (700° F), decreased less than 33 percent.

TABLE 7.16—TENSILE PROPERTIES OF IRRADIATED, ARC-MELTED, CRYSTAL BAR HAFNIUM AT 25° C (77° F), 149° C (300° F) AND 371° C (700° F)—MATERIAL HEATED FOR 1 HR AT 700° C PRIOR TO IRRADIATION

| Test temp. | Yield strength (psi $\times 10^{-3}$) | | Tensile strength (psi $\times 10^{-3}$) | Total elong (%) | Reduction in area (%) |
|-----------------------------------|--|-------|--|-----------------|-----------------------|
| | 0.2% | 0.5% | | | |
| 25° C (77° F) ¹ ----- | 67. 0 | 72. 0 | 81. 9 | 18. 9 | 25. 1 |
| 149° C (300° F) ₂ ---- | 57. 2 | 59. 9 | 63. 2 | 23. 4 | 37. 1 |
| 371° C (700° F) ₃ ---- | 36. 5 | 37. 5 | 39. 5 | 24. 3 | 38. 1 |

¹ Average of three tests.

² Average of two tests.

Creep Properties

A summary of the available information on the creep properties of crystal bar hafnium is presented in Figure 7.18 where stress is plotted against minimum creep rate [39]. Three temperatures, 260° C (500° F), 370° C (700° F), and 399° C (750° F), are represented. Data pertaining to crystal bar zirconium [49] and Zircaloy [50] are presented for comparison. Several important conclusions may be drawn from these curves:

- (1) At a given test temperature and stress level, the minimum creep rate is lower for longitudinal samples than it is for transverse samples.

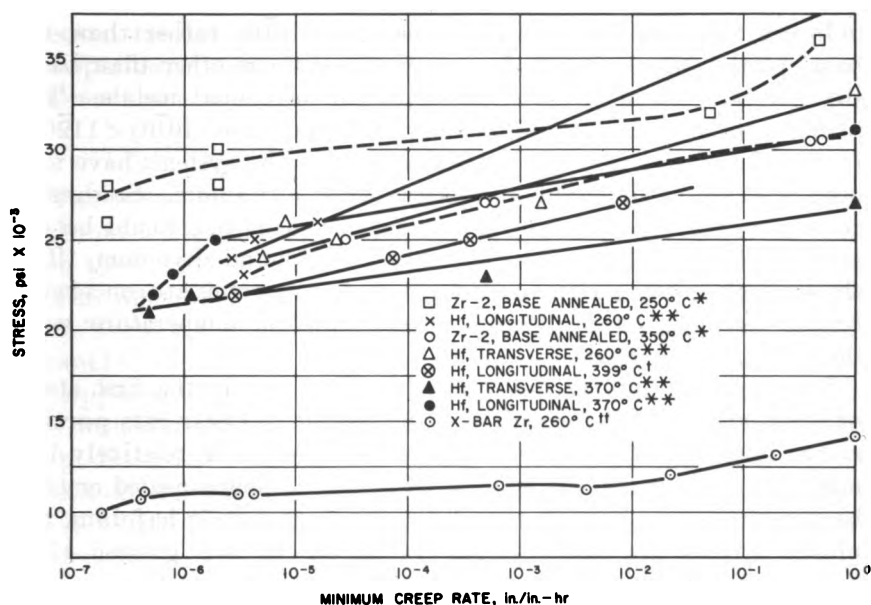


FIGURE 7.18. Creep Properties of Hafnium, Zirconium, and Zircaloy-2: (*) Forged at 927°C , Extruded at 871°C , Swaged, then Annealed for 20 Hours in Vacuum at 750°C , (**) Forged at 890°C , Rolled at 927°C , then Held at 927°C in Argon for 15 Minutes (\dagger) Forged at 1095°C , Rolled at 980°C , then Annealed for 20 Hours in Vacuum at 900°C , ($\dagger\dagger$) Hot Forged and Rolled at 760°C , Cold Rolled 10 Percent, then Annealed for 20 Hours in Vacuum at 750°C [from Refs. 39, 49 (Courtesy of the American Society for Testing Materials), and 50].

- (2) There is a definite lack of temperature dependence of the stress to cause a minimum creep rate of 10^{-6} to 10^{-5} in./in./hr.
- (3) The stress values plotted as representing a minimum creep rate of 1 in./in./hr. represent ultimate tensile strengths at temperatures corresponding to the temperatures of the creep tests. The creep data appear to extrapolate to these values.
- (4) For each set of creep data, the nominal stresses in the region of normal engineering design creep rate, 10^{-6} in./in./hr, are above the respective yield strengths. Therefore, it is not expected that the creep properties of hafnium at the temperatures discussed here would be limiting in most designs.
- (5) The stress associated with a minimum creep rate of 10^{-6} in./in./hr for hafnium is approximately twice that for crystal bar zirconium at 260°C (500°F). The creep strength of hafnium is, however, essentially the same as that of Zircaloy-2 at a given temperature.

It is expected that the creep properties of hafnium should be quite similar to those of zirconium and titanium. All three metals, hafnium, zirconium, and titanium, have less than ideal c/a ratios. This

indicates that the close-packed planes are $\{10\bar{1}0\}$ rather than the basal planes, which allows for many slip systems other than basal slip normally connected with close-packed hexagonal metals. The primary slip system in titanium and zirconium is the $(10\bar{1}0) < 11\bar{2}0 >$ [31]. Many secondary slip systems and twinning systems have also been observed in zirconium and particularly in titanium. Studies of the slip systems in hafnium have yet to be made but would be expected to be the same as those found in titanium and zirconium. The three metals in this group, as far as strength properties are concerned, behave as though the allotropic transformation temperature were the melting temperature.

Large plastic deformation during loading and in the first stage of creep make any deformation in the second or linear rate portion rather insignificant. The deformation is large even at relatively low minimum creep rates. This is found in both alpha-annealed crystal bar zirconium and Zircaloy-2 and Zircaloy-3, though in hafnium, the plastic strains are much larger (a factor of ~ 2 greater than Zircaloy-2).

The rate-controlling mechanism for creep in hafnium at these intermediate temperatures is likely to be the nucleation of cross slip or the intersection of dislocations. The high temperature creep mechanism such as dislocation climb would probably be insignificant at these temperatures since this latter mechanism is generally operative at temperatures above one-half the absolute melting point or, possibly for metals in this group, above one-half the absolute transition temperature. In general, the application of a creep rate law, such as that proposed by G. Schoeck [51] which would allow extrapolation of existing data, is rather difficult for any material, particularly with only a limited amount of data, and therefore has not been attempted.

Fatigue Properties

The fatigue properties of hafnium were determined on un-notched and notched specimens at room temperature [39] and 700° F. All specimens were machined from rolled plate 0.230 inch thick, taken both parallel with and perpendicular to the rolling direction of the plate.

Specimen Preparation

Approximately 15 mils of material were machined from each surface of the rolled plate, thus producing specimen blanks approximately 0.200 inch thick. Although some of the specimens tested were used with the as-machined surface, a number of specimens were carefully polished after machining to remove all machining marks. Still other specimens were ground and polished before testing. All notched specimens were fabricated by grinding and were carefully

checked for dimensional accuracy following the grinding operation. All specimens were vacuum-annealed at 865° C (1,600° F) following the machining and grinding operation.

Specimen Dimensions

The following pertinent dimensions apply to both the un-notched and notched specimens. The un-notched specimens were 0.195–0.200 inch thick and 0.375 inch wide at the minimum reduced section.

The dimensions for the notched specimens were essentially the same as those for the un-notched specimens, except for a 60° V-notch ground 0.015 inch deep with a root radius of 0.005 inch. Two notches, on opposite sides of each specimen, were ground perpendicular to the width of the specimen at the minimum reduced section (0.375-inch dimension). Based on Neuber's theory and corrected by the Mises criterion for failure, a theoretical stress concentration factor (K_t) of 2.57 was produced in the notched specimen with the above dimensions.

Fatigue Testing Equipment

The machine used for conducting all tests in this investigation was a SF2 constant force testing machine. The machine was adjusted to produce a completely reversed stress cycle. While in operation the machine applies a completely reversed bending moment to the specimen which is loaded as a cantilever beam. The alternating force is produced by controlling an adjustable unbalanced weight rotating at a fixed speed of 180 cycles per minute, calibrated to produce the desired constant force. All elevated temperature tests were conducted on the same machine utilizing a globar furnace partially surrounding each specimen at the test section controlled to ± 30 F° of the test temperature by a thermoelectric controller.

Test Results and Discussion

A summary of the fatigue properties of hafnium are shown in Tables 7.17 and 7.18 and plotted in the form of conventional S-N curves in Figures 7.19 to 7.22 (stress versus logarithm of the number of cycles to failure). Table 7.19 shows the strength reduction factor (K_f)³ of hafnium at 2×10^7 cycles. In evaluating the relative notch sensitivity "q" for a given material, the following relation is usually employed: $q = \frac{K_f - 1}{K_t - 1}$. The closer "q" approaches unity, the more notch sensitive the material. Most engineering materials show values less than one. Tables 7.20 and 7.21 show the "q" values for a number of engineering materials for comparative purposes.

³ K_f = the fatigue strength of an un-notched specimen divided by the fatigue strength of a notched specimen at an equal number of cycles.

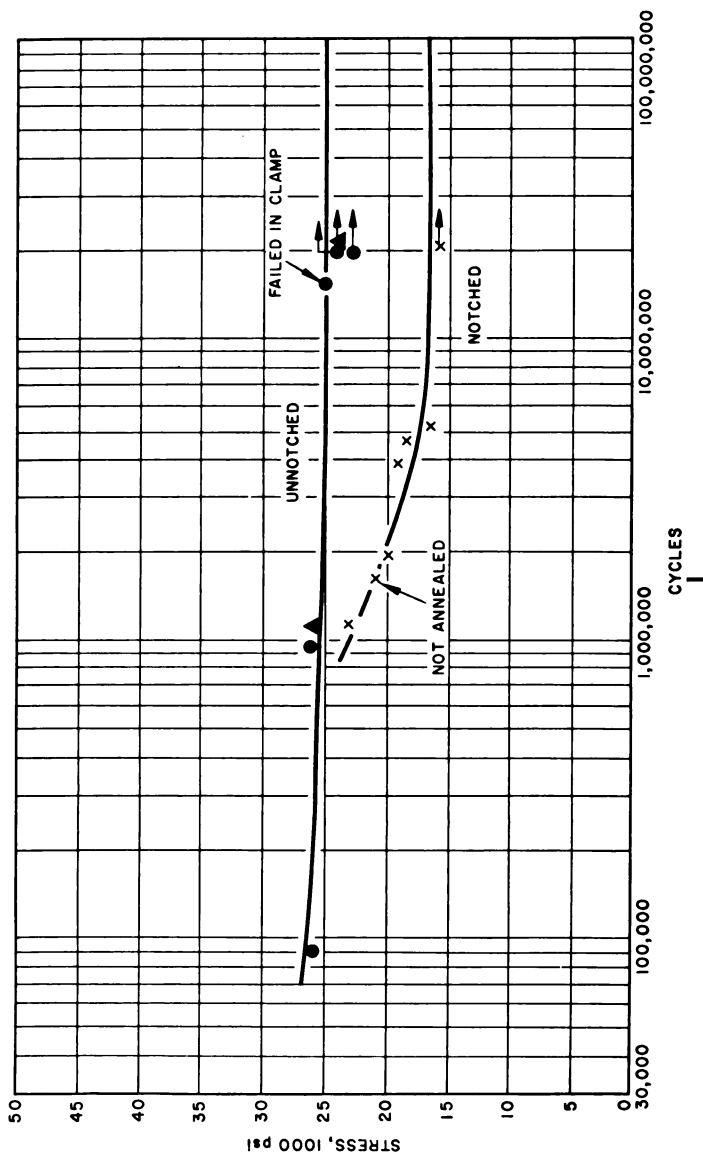


FIGURE 7.19. Room Temperature Fatigue Test Data for Hafnium (Longitudinal).

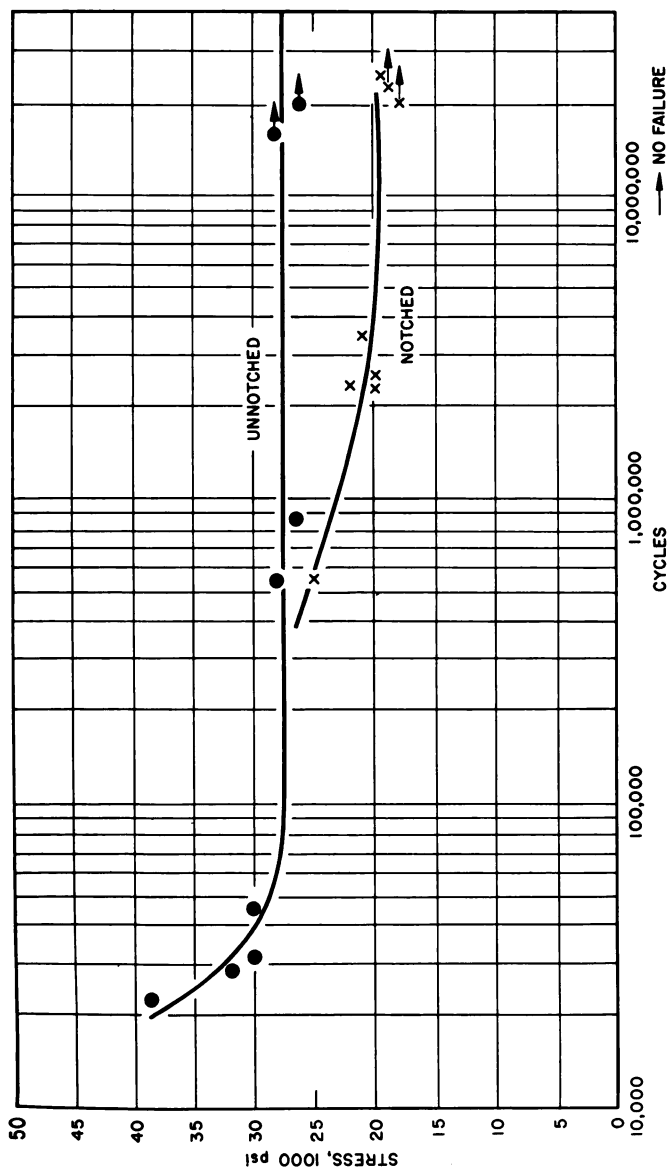


FIGURE 7.20. Room Temperature Fatigue Test Data for Hafnium (Transverse).

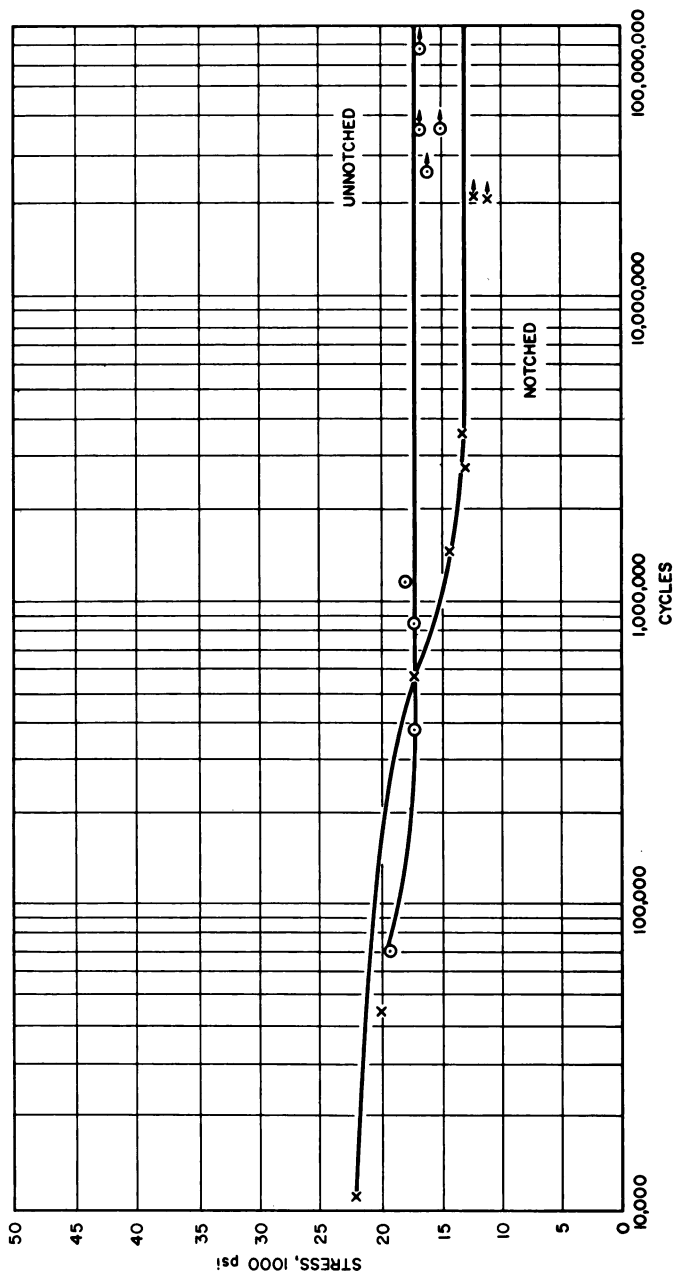


FIGURE 7.21. Fatigue Test Data for Hafnium at 371° C (700° F) (Longitudinal).

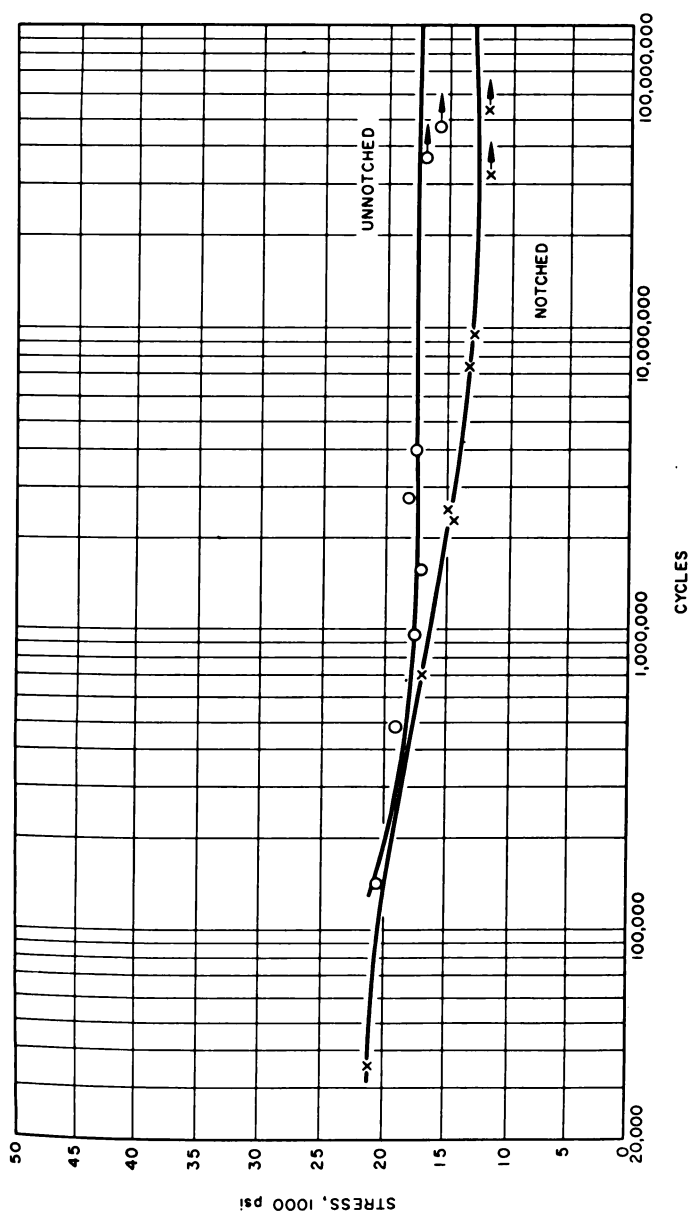


FIGURE 7.22. Fatigue Test Data for Hafnium at 371° C (700° F) (Transverse).

Another ratio frequently employed in evaluating un-notched fatigue properties for steels is the endurance or fatigue ratio which is the ratio of the un-notched endurance strength to the tensile strength. For most ferrous alloys, the value is approximately 0.5. Relative values of this ratio for a number of engineering materials as compared with hafnium have been included in Tables 7.20 and 7.21. It can be seen that this ratio for hafnium is approximately the same as that for steel.

It might be well to comment briefly on the two basic methods of conducting fatigue tests and the type of information that can be obtained from each type of test. One type of fatigue test is the constant load test in which the load remains constant during the entire life of the specimen; the second type of test is the constant deflection test wherein the deflection is held constant by varying the load.

TABLE 7.17—FATIGUE TESTS OF HAFNIUM (TRANSVERSE)

| Stress (psi) | Cycles to failure | Surface | Stress (psi) | Cycles to failure | Surface |
|-------------------------|-------------------------|---------------|-------------------|-------------------------|----------------------|
| Un-notched—Test at R.T. | | | Un-notched—700° F | | |
| 38,500 | 23,000 | Polished. | 20,000 | 145,000 | Ground and polished. |
| 32,000 | 29,000 | Do. | 18,000 | 2,804,000 | Do. |
| 28,000 | ¹ 15,900,000 | Do. | 16,000 | ¹ 46,000,000 | Do. |
| 30,000 | 31,000 | Rough ground. | 19,000 | 477,000 | Do. |
| 30,000 | 44,000 | Do. | 17,000 | ¹ 36,000,000 | Do. |
| 26,000 | ¹ 20,318,000 | Do. | 18,000 | 952,000 | Do. |
| 28,000 | 535,000 | Do. | 17,500 | 388,000 | Do. |
| 27,000 | 850,000 | Do. | 17,500 | 1,596,000 | Do. |
| Notched—R.T. | | | Notched—700° F | | |
| 22,000 | 2,416,000 | | 17,200 | 695,000 | |
| 20,000 | 2,384,000 | | 15,000 | 2,520,000 | |
| 18,000 | ¹ 20,000,000 | | 14,800 | 2,300,000 | |
| 25,000 | 539,000 | | 13,000 | 9,420,000 | |
| 20,000 | 2,484,000 | | 12,000 | ¹ 30,880,000 | |
| 19,000 | ¹ 23,000,000 | | 13,500 | 7,414,000 | |
| 21,000 | 3,450,000 | | 12,000 | ¹ 51,000,000 | |
| 19,500 | ¹ 25,250,000 | | 21,000 | 37,000 | |

¹ No failure.

TABLE 7.18—FATIGUE TESTS OF HAFNIUM (LONGITUDINAL)

| Stress (psi) | Cycles to failure | Surface | Stress (psi) | Cycles to failure | Surface |
|-----------------|---------------------------|---------|-------------------|---------------------------|----------------------|
| Un-notched—R.T. | | | Un-notched—700° F | | |
| 26, 600 | 88, 000 | Ground. | 17, 000 | 385, 000 | Ground and polished. |
| 23, 000 | ¹ 20, 000, 000 | Do. | 15, 000 | ¹ 36, 000, 000 | Do. |
| 24, 000 | 20, 000, 000 | Do. | 19, 000 | 72, 000 | Do. |
| 26, 000 | 1, 070, 000 | Rough. | 16, 000 | 25, 880, 000 | Do. |
| 24, 000 | ¹ 20, 700, 000 | Do. | 16, 500 | 36, 000, 000 | Do. |
| 25, 000 | ¹ 15, 227, 000 | Ground. | 16, 500 | 68, 000, 000 | Do. |
| 26, 000 | ² 932, 000 | Do. | 18, 000 | 1, 186, 000 | Do. |
| Notched—R.T. | | | Notched—700° F | | |
| 19, 000 | 3, 826, 000 | | 17, 000 | 570, 000 | |
| 16, 000 | ¹ 20, 000, 000 | | 13, 000 | 3, 590, 000 | |
| 17, 000 | 5, 133, 000 | | 22, 000 | 11, 000 | |
| 18, 000 | 44, 390, 000 | | 11, 000 | ¹ 2, 045, 000 | |
| 21, 000 | ¹ 1, 571, 000 | | 12, 000 | ¹ 21, 000, 000 | |
| 23, 000 | 1, 120, 000 | | 14, 000 | 14, 116, 000 | |
| 20, 000 | 1, 835, 000 | | 20, 000 | 44, 000 | |
| | | | 12, 750 | 2, 722, 000 | |

¹ No failure.² Failed in grips.³ Not annealed.TABLE 7.19—SUMMARY OF FATIGUE PROPERTIES OF HAFNIUM
(2 x 10⁷ CYCLES)

| Specimen type | Test temper- ature (° F) | Fatigue strength at 2 x 10 ⁷ cycles (psi) | T.S. (psi) | K _f | Endurance ratio | q |
|--|-----------------------------------|--|---------------|----------------|--------------------|-------|
| TESTED TRANSVERSE TO ROLLING DIRECTION | | | | | | |
| Un-notched..... | R.T. | 27, 500 | 55, 000 | ----- | 0. 50 | ----- |
| Do..... | 700 | 17, 500 | 27, 000 | ----- | 0. 65 | ----- |
| Notched..... | R.T. | 19, 500 | ----- | 1. 41 | ----- | 0. 23 |
| Do..... | 700 | 12, 500 | ----- | 1. 40 | ----- | 0. 23 |
| TESTED PARALLEL TO ROLLING DIRECTION | | | | | | |
| Un-notched..... | R.T. | 25, 000 | 57, 200 | ----- | 0. 435 | ----- |
| Do..... | 700 | 17, 000 | 31, 000 | ----- | 0. 550 | ----- |
| Notched..... | R.T. | 16, 500 | ----- | 1. 52 | ----- | 0. 26 |
| Do..... | 700 | 12, 500 | ----- | 1. 36 | ----- | 0. 19 |

TABLE 7.20—FATIGUE DATA FOR ZIRCONIUM AND ZIRCONIUM ALLOYS [31]¹

| Materials | Test temperature (° C) | Tensile strength (psi) | Fatigue strength 10 ⁷ cycles (psi) | | Fatigue ratio | K, 10 ⁷ cycles | q |
|--|------------------------|------------------------|---|---------------------|---------------|---------------------------|-------|
| | | | Un-notched | Notched | | | |
| Zr Iodide..... | R.T. | 33,300 | 21,000 | 8,000 | 0.63 | 2.6 | ----- |
| Zr Iodide..... | 400 | 12,800 | 10,500 | 6,500 | 0.82 | 1.6 | ----- |
| Zr Iodide..... | R.T. | 93,700 | 56,000 | 12,000 | 0.60 | 4.7 | ----- |
| Zr Iodide 0.3 w/o O ₂ | 400 | 22,400 | 15,000 | 6,000 | 0.67 | 2.5 | ----- |
| 1 Zr 2.2 w/o Sn..... | 400 | 21,100 | 18,000 | 8,000 | 0.85 | 2.3 | ----- |
| Sponge Zr 2.5 w/o Sn 0.14% O ₂ | 400 | 31,500 | 24,000 | 8,000 | 0.76 | 2.6 | ----- |
| Zircaloy-2 beta-quenched and alpha-annealed..... | 316 | 34,400 | ² 27,500 | ² 11,000 | 0.80 | 2.5 | 0.60 |
| Base annealed..... | 316 | 16,300 | 28,000 | 9,000 | 0.87 | 3.1 | 0.85 |

¹ Courtesy of B. Lustman and F. Kerze, Jr., Addison Wesley, and the USAEC.² These values represent 10⁸ cycles.TABLE 7.21—FATIGUE DATA FOR SEVERAL ENGINEERING MATERIALS [31]¹

| Material | Test temperature | Tensile strength (lb/in. ²) | Fatigue ratio | q |
|-------------------------|------------------|---|---------------|------|
| 24 ST-Al Alloy..... | R.T. | 69,900 | 0.37 | 0.61 |
| FS 1 Mg..... | R.T. | 40,100 | 0.47 | 0.64 |
| SAE 2330..... | R.T. | 150,000 | 0.50 | 1.88 |
| 18-8 Stainless..... | R.T. | 210,000 | 0.52 | 2.16 |
| Com. Pure Titanium..... | R.T. | 64,000 | 0.80 | 0.45 |
| SAE 4340..... | R.T. | 150,000 | 0.49 | 1.56 |

¹ Courtesy of B. Lustman and F. Kerze, Jr., Addison Wesley, and the USAEC.

In the former test, the stress cycle may vary considerably depending upon the work hardening properties of the material. Furthermore, with the initiation of the first crack in a constant load test, the crack propagates at an increasing rate with each ensuing cycle, whereas in the constant deflection test, the load decreases once the crack has been initiated. Usually the results of both types of test are comparable at relatively low stresses. However, with the advent of numerous engineering applications in which the life of a component may be limited to a relatively few cycles, it is obvious that the type of fatigue data used for a particular design is of extreme importance. From these general considerations it is evident that the method of fatigue testing is an important consideration, particularly with materials such as hafnium which show a relatively high work harden-

ing rate. Consequently, if hafnium should be used under conditions of constant deflection (especially high deflections) then tests of this type should be given adequate consideration.

In summarizing the limited data obtained in this study and considering the test method, the following general statements can be made:

- (1) Specimens tested parallel to the rolling direction have slightly lower fatigue properties than specimens tested transverse to the rolling direction.
- (2) The fatigue properties of hafnium at 700° F are considerably lower than those at room temperature.
- (3) Although the notches employed decreased the fatigue properties appreciably, the strength factor (K_f) is considerably lower than the theoretical stress concentration factor (K_t) indicating that hafnium has relatively low notch sensitivity for the particular notch and test method employed.
- (4) Hafnium exhibits a fatigue notch sensitivity value "q" which is generally lower than most engineering materials.
- (5) Relatively small differences in fatigue strength of hafnium occur as a result of surface preparation.
- (6) Inasmuch as hafnium cold works readily, it would be of value to compare the fatigue properties of hafnium tested by a constant deflection method with those obtained in this study by the constant load method.

Modulus of Elasticity [39]

The modulus of elasticity was determined on hafnium specimens cut parallel with the direction of rolling at three temperatures—70, 500, and 700° F [39]. The values obtained are shown in Table 7.22.

TABLE 7.22—MODULUS OF ELASTICITY OF HAFNIUM

| <i>Temperature (°F)</i> | <i>Modulus of elasticity (psi)</i> |
|-------------------------|------------------------------------|
| 70..... | 19.8×10^6 |
| 500..... | 15.4×10^6 |
| 700..... | 13.8×10^6 |

7.4 PHYSICAL METALLURGY AND METALLOGRAPHY

By K. M. Goldman *

Preferred Orientations in Hafnium

Deformation characteristics of hafnium have been studied by Epelsheimer and Gould [52]. In their earlier studies, these investigators were limited by the fact that the material available for their

* Westinghouse Atomic Power Division.

study (crystal bar) showed edge cracking when it was cold rolled more than 30 percent without intermediate annealing. It was found, however, that at slightly elevated temperatures the material was plastic enough to be deformed by compression as much as 90 percent total reduction. The compression texture after 78 percent compression was found to be $[0001]$ rotated $15\text{--}30^\circ$ from the axis of compression. The rolling texture is very similar to the compression texture, the (0001) plane being rotated $10\text{--}25^\circ$ around a $[10\bar{1}0]$ rotational axis. It was also observed that, since considerable spreading occurred during rolling at 500°C , this deformation may be analogous to compression deformation. These investigators accounted for the texture observed by $(11\bar{2}2)$ and $(11\bar{2}1)$ twinning and $(10\bar{1}2)$ twinning, wherein the hexagonal axis is rotated from the compression axis, and by $\{0001\} \langle 11\bar{2}0 \rangle$ and $\{10\bar{1}1\} \langle 11\bar{2}0 \rangle$ slip.

A more extended study of the cold rolled texture of hafnium was performed by these same investigators [53]. In this work arc melted crystal bar containing 3 w/o zirconium was used. An interesting feature of this work, although not related directly to it, is that zirconium in solid solution in hafnium does not impair its cold rolling properties. Other material containing only 0.01 w/o zirconium cracked at 60–70 percent total reduction in thickness. This, however, was attributed to the presence of dissolved gases.

The purpose of the latter study was to determine the cold rolled texture of hafnium and to compare this texture with that of other hexagonal metals with c/a ratios near to but less than 1.63; that is, titanium, zirconium, and beryllium. These data are summarized in Table 7.23.

TABLE 7.23—COLD-ROLLED TEXTURES OF SOME HEXAGONAL METALS WITH SIMILAR c/a RATIOS [53]¹

| Metal | c/a ratio | Direction parallel to rolling direction | Angle between basal plane and rolling plane in transverse direction ($^\circ$) |
|----------------|-------------|---|--|
| Titanium..... | 1. 60 | $[10\bar{1}0]$ | 40 ± 10 |
| Zirconium..... | 1. 59 | $[10\bar{1}0]$ | 38 ± 2 |
| Beryllium..... | 1. 58 | $[10\bar{1}0]$ | 0 ± 65 |
| Hafnium..... | 1. 58 | $[10\bar{1}0]$ | 25 ± 2 |

¹ Courtesy of the Institute of Metals.

Typical pole figures obtained by Eppelsheimer and Gould are shown in Figure 7.23. Only the inner 60° was determined because of the fact that hafnium is poorly suited for transmission techniques.

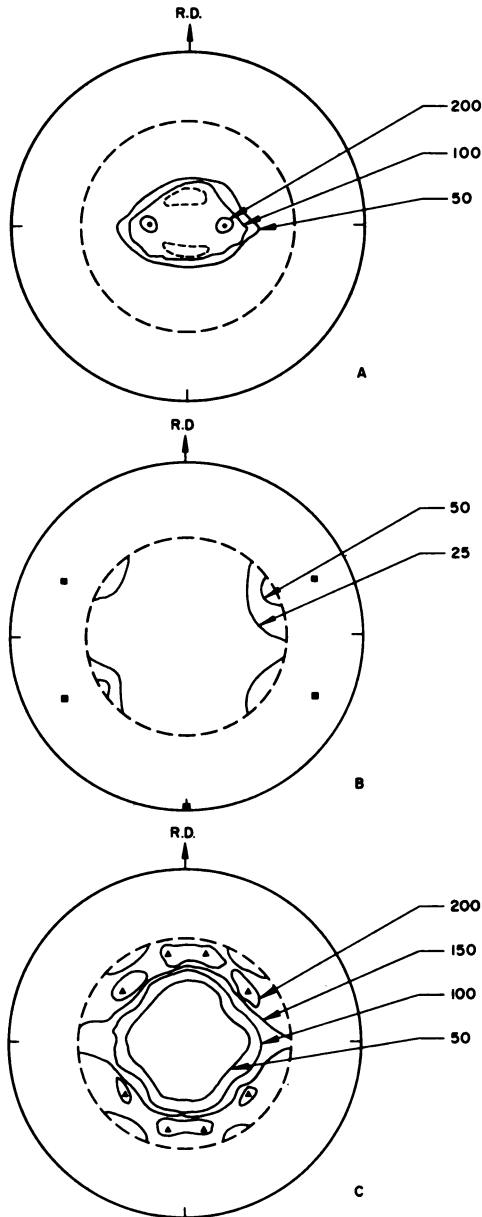


FIGURE 7.23. Pole Figures for Hafnium Strip Containing 3 Percent Zirconium Cold Rolled to 95 Percent Reduction in Thickness; (a) (0002) Dotted Lines Indicate Spurious Areas; (b) (1010); (c) (1011). Scale Is Counts Per Second after Correction for Tilting Factor (from Ref. 53 Courtesy of the Institute of Metals).

The (0002) pole figure contains two extraneous peaks, shown by dotted lines, which arise because 20 angles for (0002) and $(10\bar{1}1)$ are less than 2° apart.

The theoretical locations of the peaks, assuming a basal rotation of 25° toward the transverse direction about an axis in the rolling direction from an ideal (0001) $[10\bar{1}0]$ texture is indicated by small dots, squares, and triangles in the (0002), $(10\bar{1}0)$, and $(10\bar{1}1)$ pole figures, respectively.

The symmetry of the $(10\bar{1}0)$ and $(10\bar{1}1)$ pole figures is well defined which indicates that the deformed sample assumes a $[10\bar{1}0]$ direction. The (0002) peak appears to lie at an angle of 25° with the rolling plane rotated about the rolling direction, which is the $[10\bar{1}0]$ direction. Although the width of the peak itself and the possibility of very small variations in the tilting angle intensity corrections precluded the absolute determination of the exact angle of rotation, it seems logical to assume that the rotation is $25 \pm 2^\circ$. It is believed that the mechanism for the formation of this deformation texture is similar to that described for other metals of similar c/a ratio.

Very recently, the rolling and annealing textures of hafnium sheet were determined by Keeler [54]. Crystal bar hafnium containing less than 3 w/o zirconium was used. The deformation texture of 70 percent cold rolled hafnium was similar to that reported previously by Eppelsheimer and Gould. Hafnium sheet annealed in vacuo for 1 hour at 800°C and 1 hour at $1,100^\circ\text{C}$ exhibited $[10\bar{1}0]$ pole concentrations which were no longer in the rolling direction. Although no unique texture can be derived from Keeler's pole figures, two possible orientation descriptions are as follows: (1) $[10\bar{1}0]$ directions in the rolling plane 25° from the rolling direction with the basal plane tilted about 20° in the transverse direction; and (2) $[10\bar{1}0]$ directions rotated 30° from the rolling direction about an axis 25° in transverse direction from the normal to the sheet.

Recrystallization Studies

Litton [4] reported that samples of iodide hafnium were annealed in an argon atmosphere for 1 hour at temperatures of 500 to 800°C after being cold rolled to a 65 percent reduction in thickness. Subsequent hardness measurements and metallographic examination yielded the data on the recrystallization behavior summarized in Table 7.24. The data indicate that the temperature range over which recrystallization takes place in 65 percent cold reduced iodide hafnium is $700\text{--}800^\circ\text{C}$. There appears to have been no definitive study of recovery and recrystallization.

Additional studies of the effect of annealing at a series of temperatures on the hardness of arc melted iodide hafnium were per-

TABLE 7.24—DATA FOR DETERMINING RECRYSTALLIZATION TEMPERATURE IN IODIDE HAFNIUM COLD WORKED 65 PERCENT [4]¹

| Annealing temperature (° C) | Hardness (P _B) | Structure |
|-----------------------------|----------------------------|------------------------|
| 500----- | 104 | Cold worked. |
| 600----- | 99 | Do. |
| 700----- | 93 | Partly recrystallized. |
| 800----- | 88 | Recrystallized. |

¹ Courtesy of the Electrochemical Society.

formed at Bettis Atomic Power Division by Castleman *et al.* [16]. The material was heated for 1 hour in vacuum after cold rolling to 9, 19, 31, 49, and 65 percent reduction in thickness. The results are shown in Figure 7.24, where the hardness resulting from the various annealing treatments is shown for each of the cold reduced strips. The hardness of the 9 percent cold reduced material decreases very gradually, and there is no indication that recrystallization has taken place under these particular conditions. No sharp drop in hardness is exhibited by the curve for the 19 percent cold reduced material. The curves for the material cold reduced 31, 49, and 65 percent indicate that recrystallization might have occurred near 800° C. Unfortunately, no metallographic study was made.

A recent metallographic and hardness study has been made at Bettis [55] on arc melted iodide hafnium strip which was annealed for 1 hour at 927° C (1,700° F) and then cold rolled 16 percent. Samples cut from this strip were heat treated as follows:

- (1) 700° C for 1, 3, 8, and 30 hours.
- (2) 800° C for 1 hour.
- (3) 900° C for 1 hour.
- (4) 1,000° C for 1 hour.

Hardness values were obtained and metallographic observations were made after each of these treatments. Hardness values are shown in Table 7.25, and microstructures are shown in Figures 7.25

TABLE 7.25—HARDNESS (DPH-50 Kg LOAD) OF ARC MELTED CRYSTAL BAR HAFNIUM STRIP AFTER INDICATED HEAT TREATMENTS

ANNEALED 1 HR AT 927° C (1,700° F)—DPH 134, COLD ROLLED 16%—DPH 195

| Temperature (° C) | Time (hr) | | | |
|-------------------|-----------|-------|-------|-------|
| | 1 | 3 | 8 | 30 |
| 700----- | 151 | 145 | 142 | 134 |
| 800----- | 149 | ----- | ----- | ----- |
| 900----- | 146 | ----- | ----- | ----- |
| 1, 000----- | 142 | ----- | ----- | ----- |

to 7.30. Qualitatively, it appears that, for hafnium cold reduced 16 percent, recrystallization starts at 700° C (3 hr) and is complete between 800 and 900° C. These results are in agreement with previous results.

Further microstructural evidence of recrystallization behavior is indicated in the work of Roth [56] in which hafnium crystal bar produced by the Phillips Company (The Netherlands) was employed. Typical microstructures of as-deposited crystal bar having two different zirconium contents are shown in Figure 7.31. Microstructures of the same material after reduction in area of 75 percent by cold

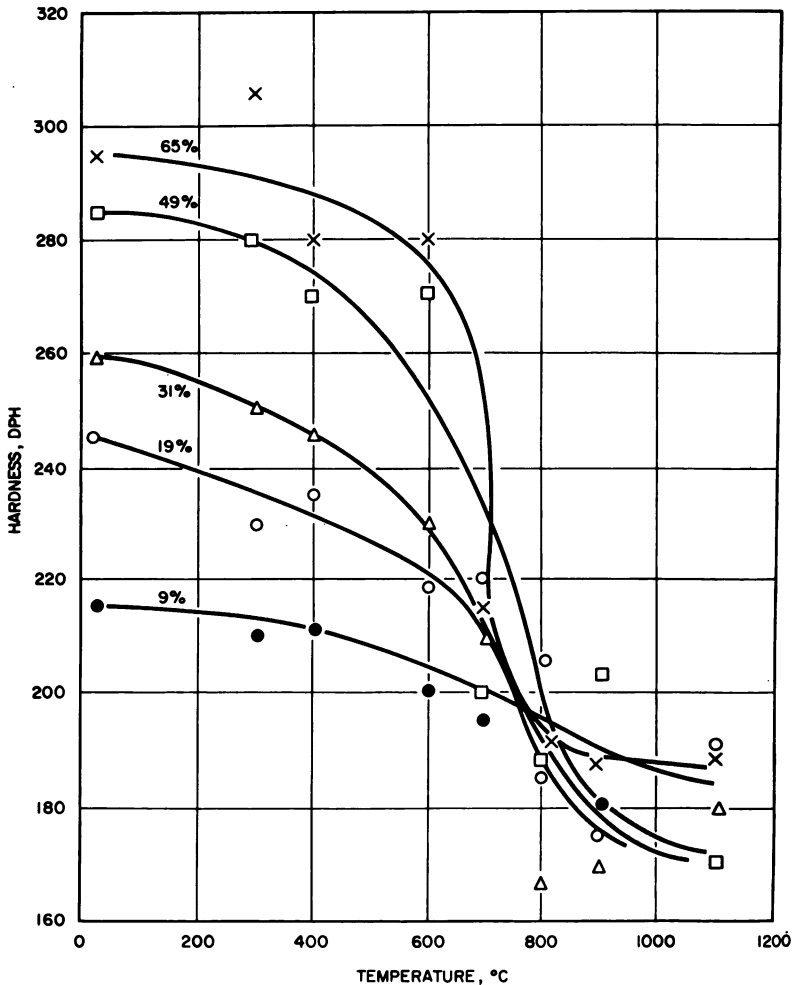


FIGURE 7.24. The Variation of Hardness with Temperature for Arc-Melted Iodide Hafnium Cold Rolled from 9 to 65 Percent and Heated for 1 Hour at Temperatures from 200 to 1,100° C.



FIGURE 7.25. Hafnium Strip, Cold Reduced 16 Percent; Electropolished for 5-30 Seconds at a Current Density of 0.015 Amp in a Solution Containing 600 cc Methyl Alcohol, 60 cc Perchloric Acid (60 Percent), 360 cc Ethylene Glycol Monobutyl Ether, and 2 cc of Inhibitor Solvent "X"; 250X, Polarized Light.

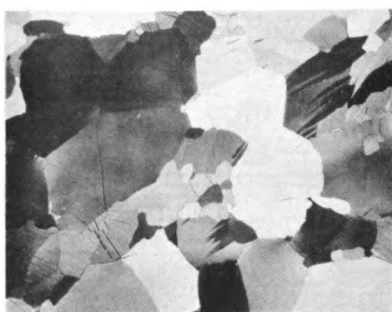


FIGURE 7.27. Hafnium Strip, Cold Reduced 16 Percent; Heated at 700° C for 3 Hours; Electropolished as in figure 7.25; 250X, Polarized Light.

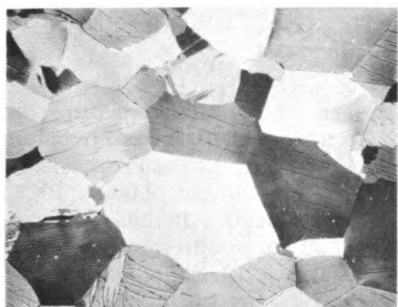


FIGURE 7.26. Hafnium Strip, Cold Reduced 16 Percent; Heated at 700° C for 1 Hour; Electropolished as in figure 7.25; 250X, Polarized Light.

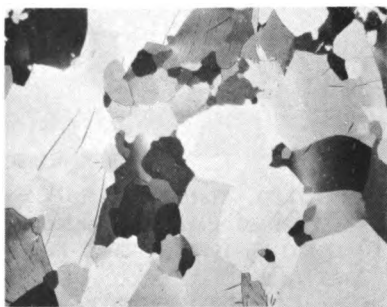


FIGURE 7.28. Hafnium Strip, Cold Reduced 16 Percent; Heated at 800° C for 1 Hour; 250X, Polarized Light.

(Photomicrographs on this page reduced 55½ % in printing.)

swaging and annealing for 2 hours at 500, 800, and 1,100° C are shown in Figures 7.32 and 7.33. (The as-swaged structures, not shown, are essentially the same as that shown for the material annealed at 500° C.) It is evident that under the conditions prevailing, recrystallization begins at a temperature between 800 and 1,100° C—somewhat higher than indicated by Litton [4]. Similarly treated crystal bar containing 24 w/o zirconium was shown by Roth to be fully recrystallized after 2 hours at 800° C.



FIGURE 7.29. Hafnium Strip, Cold Reduced 16 Percent; Heated at 900° C for 1 Hour; 250X, Polarized Light.

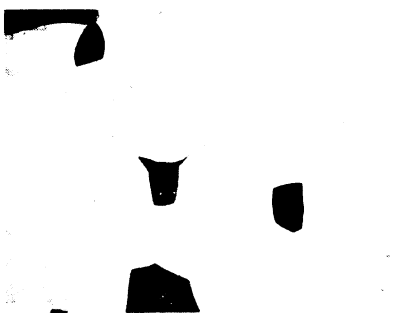


FIGURE 7.30. Hafnium Strip Cold Reduced 16 Percent; Heated at 1000° C for 1 Hour; 250X, Polarized Light.

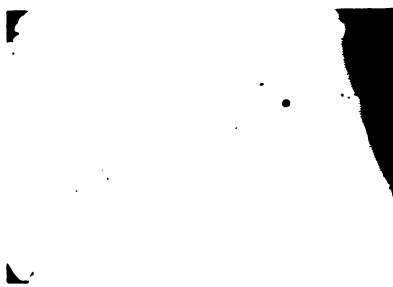


FIGURE 7.31. Microstructure of Hafnium and Hafnium-Zirconium Crystal Bar, As-Deposited. Top: Hafnium, Bright Light, 100X, Longitudinal. Bottom: Hafnium+2 w/o Zirconium, Bright Light, 100X, Longitudinal.

(Photomicrographs on this page reduced 55½% in printing.)

Metallography of Hafnium

The metallography of hafnium is quite similar to that of zirconium and titanium. The precautions used for cutting and for preliminary polishing on abrasive papers apply equally well to all three materials. Therefore, the discussions in this section, although aimed at hafnium, will, to those readers who are familiar with zirconium and titanium, appear quite applicable to these other metals.

Probably the most significant advancement in the metallography of hafnium as well as zirconium in recent years is the chemical polish-etch methods developed by Cain [58, 59]. Prior to this development, three other methods had been used with varying degrees of success. These are the mechanical [60, 61], the attack-polish [62], and the electrolytic methods [56, 57, 63], and they are summarized in Table 7.26.

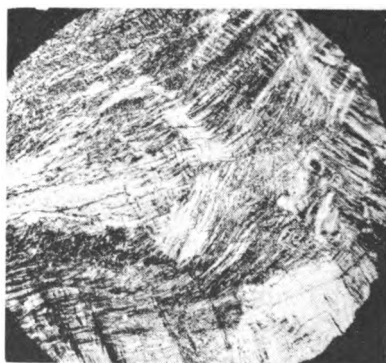
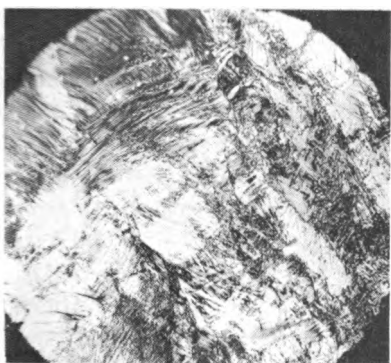
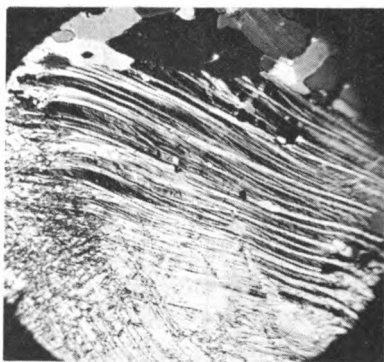
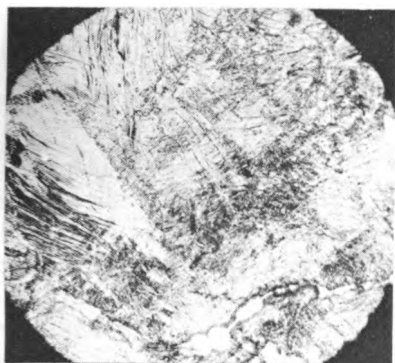
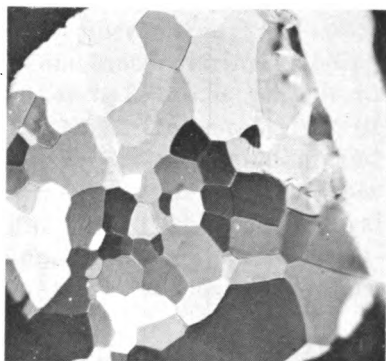
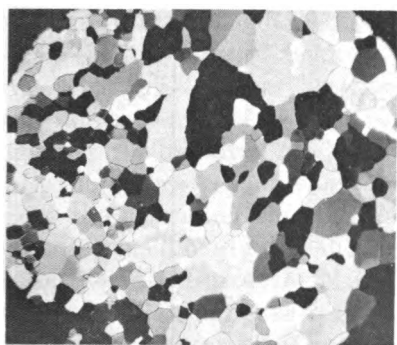


FIGURE 7.32. Structures Resulting from Annealing Hafnium (Trace of Zirconium) 2 Hours at Indicated Temperatures and Water Quenching. Electrolytically Polished in a 100 to 5-6 (Volumetric Ratio) of Glacial Acetic Acid to Perchloric Acid; 0.4 Amp, 18 v; 250X, Transverse, Polarized Light. Top; 1,100° C. Middle: 800° C. Bottom: 500° C.

FIGURE 7.33. Structures Resulting From Annealing Hafnium (2 w/o Zirconium) for 2 Hours at Indicated Temperatures and Water Quenching; Same Polishing Method as that of figure 7.32; 250X, Transverse, Polarized Light. Top: 1,100° C. Middle: 800° C. Bottom: 500° C.

(Photomicrographs on this page reduced 50% in printing.)

TABLE 7.26—SUMMARY OF METALLOGRAPHIC PROCEDURES FOR HAFNIUM AND ZIRCONIUM AND THEIR ALLOYS [58]¹

| Polishing method | Used by— | Grinding step | Polishing step | Preferred etchant |
|------------------|----------------------------------|--|--|---|
| Mechanical | U.S. Bureau of Mines | 2.0 and 1 silicon carbide paper | Canvas lap—280 aluminum oxide; Felt lap—600 silicon carbide; Gamal cloth—Linde B. | 6 parts glycerine. 2 parts HF. |
| Mechanical | Argonne National Laboratory | 120, 180, 240, 400, 3/0 and 4/0 papers. | Silk lap—600 silicon carbide; Microcloth—Linde A; Microcloth—Linde B. | 1 part HNO ₃ . 5 ml HF. 3 ml HNO ₃ . 92 ml H ₂ O. |
| Mechanical | Westinghouse | 240 and 400 silicon carbide wet belts—600 silicon carbide wax lap. | Gamal lap—Linde B | 60 ml 30% H ₂ O ₂ . 30 ml HNO ₃ . |
| Attack—Polish | Sylvania Electric Products, Inc. | 180-grit belt, 2/0 and 3/0 jewelers paper on rotating disks. | Silk lap—Linde A, dilute HF; Gamal lap—Linde B, dilute HF. | 30 ml ethyl alcohol. 2 drops 48% HF. |
| Electrolytic | Massachusetts Institute of Tech. | Customary paper grinding, finishing with 3/0. | 45 sec polishing time at 0.02 to 0.5 amp in an electrolyte of 1 part 60% perchloric acid and 10 parts glacial acetic acid. | No subsequent etching. |
| Electrolytic | Jacquet | Abraded to 1/0 paper finish | 350 ml 95% ethyl alcohol. 100 ml 1.20 sp gr perchloric, 50 ml 2 butoxyethanol 10–20 sec, 30 volts. | No subsequent etching. |

¹ Courtesy of the American Society for Metals.

Hafnium is a difficult metal to prepare for microscopic examination because of its marked tendency to flow and smear during grinding and polishing. It has been reported that hafnium is difficult to etch and is sensitive to cold work by abrasion. One means [60] of insuring the removal of flowed metal is to prolong grinding and polishing times beyond that normally required to remove scratches from the preceding step. Those laboratories in which mechanical polishing methods applicable to hafnium have been developed include the U.S. Bureau of Mines [60], Argonne National Laboratory [61], and Westinghouse [61].

A novel adaptation of mechanical polishing techniques is that of Metz and Woods [62] who reduce polishing times by mixing dilute hydrofluoric acid with abrasive for the final polishing steps.

Electropolishing Techniques

Probably the most suitable electropolishing method for hafnium is that developed by Roth [56, 57]. The prescribed electrolyte is a solution of glacial acetic acid and perchloric acid in volumetric ratio of 100 to 5-6. Any emery paper polishing that is done should be carried only through 3/0 grit because any grit finer than 3/0 has a tendency to burnish rather than to remove metal. Several successive immersions in the solution, with the current on, of a few seconds duration each with continuous agitation, are much more useful in obtaining an excellent polish than is a single long-time immersion with the sample held stationary. It has been found that the most satisfactory results are obtained when a direct current of 0.4 ampere (for wires of 0.080 to 0.2 inch in diameter) and a potential difference of 18 volts are used. The results of such a technique are represented by the microstructures shown in Figures 7.32 and 7.33.

Another electrolytic polishing technique has been developed very recently by Gross at Bettis. The polishing unit used is the DISA, distributed by Addehlom Company of America, New York. The cathode is made of stainless steel and the electrolyte is composed of 600 cc of methanol, 60 cc of perchloric acid (60 percent), 360 cc of ethylene glycol monobutyl ether, and 2 cc of Inhibitor Solvent "X." A current density of 0.015 amp/mm² is used. Polishing time varies from 5 to 30 seconds. To obtain an excellent polish, a high voltage must be used since a low voltage produces an etching effect.

The preparation preliminary to electropolishing consists of grinding on a belt sander with a 320X grit belt and rough polishing on 400X and 600X grit silicon carbide paper and on 400X grit silicon carbide TRI-M-ITE polishing paper. After the sample is given a final polish on a miracloth-covered lap using a slurry of Linde B alumina and water, it is then electropolished under the conditions

mentioned above, washed in water, and dried. The chief advantage of this method is that it essentially eliminates any surface distortion. The series of photomicrographs shown in Figures 7.25 to 7.30 represents specimens polished by this method.

Chemical Polishing

This is a method developed by Cain [58, 59]. If a detailed structural study is required, the sample is given a preliminary polishing through 3/0 paper as required for the electrolytic technique. If nothing more than a routine grain size measurement is required, the sample need only be ground on a 180X grit silicon carbide paper. In either case, the sample is then swabbed with the chemical polishing solution. The various compositions which have been used are shown in Table 7.27. It is to be noted that the acid ingredients of the polishing solution work satisfactorily in glycerine, water, or hydrogen peroxide. A few seconds after the specimen has contacted the acid, nitrous oxide vapors will be emitted at the sample surface. Most samples require 5–10 seconds additional solution contact after the appearance of these brownish-yellow vapors. After this time has elapsed, the specimen should be immediately washed in cold running water and dried. If, for some reason, the specimen has not been sufficiently polished, the procedure can be repeated.

TABLE 7.27—VARIOUS CHEMICAL POLISHING COMPOSITIONS SUITABLE FOR HAFNIUM [58]¹

| <i>Polishing Solution</i> | <i>Composition</i> |
|---------------------------|--|
| A----- | 45 ml C ₃ H ₅ OH. 45 ml HNO ₃ (conc). 8–10 ml HF (48%). |
| B----- | 45 ml H ₂ O. 45 ml HNO ₃ (conc). 8–10 ml HF (48%). |
| C----- | 45 ml H ₂ O ₂ (30%). 45 ml HNO ₃ (conc). 8–10 HF (48%). |

¹ Courtesy of the American Society for Metals.

Specimens of hafnium which have been chemically polished are shown in Figure 7.34.

Cain [58, 59] states that a metallographic technique must meet four requirements: (1) reproducibility, (2) speed, (3) simplicity, and (4) versatility. All of the known methods meet these requirements in varying degrees. Mechanical polishing, which is perhaps a slower method than the rest, nevertheless can produce good results if special care is taken to avoid distorted structures. Electropolishing methods,

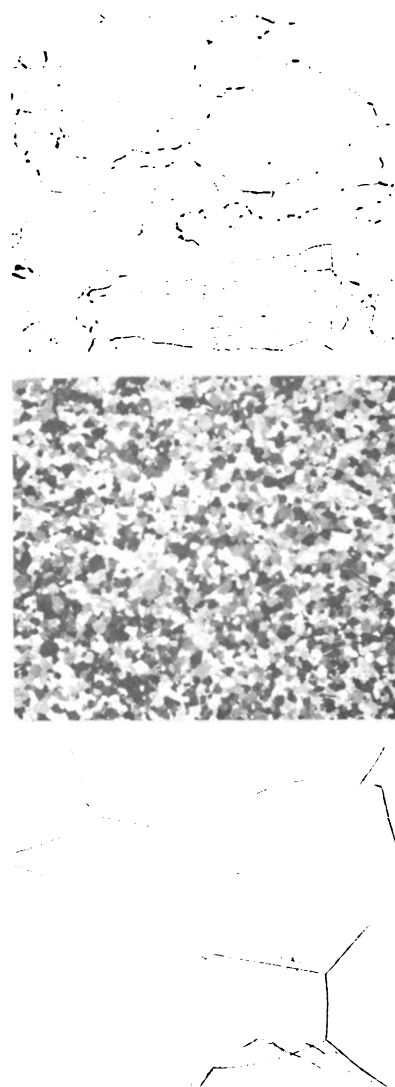


FIGURE 7.34. Hafnium Specimens Prepared by Chemical Polishing. Top: 100X, Bright Light; Hot-Rolled [64]. Middle: 100X, Polarized Light; Annealed 700° C [64]. Bottom: Hafnium, Chemically Polished in Solution B, then Cycled Between Room Temperature and 1,300° C in an Argon Atmosphere; Successive Grain Boundary Positions Revealed by Thermal Grooving Are Evident. Photographed with Bright-Field Illumination, 100X (from Ref. 58 Courtesy of the American Society for Metals).

(Photomicrographs on this page reduced 50% in printing.)

when carefully controlled, produce satisfactory results and are capable of speedy performance. One obvious disadvantage of electro-polishing with the acetic-perchloric mixture is its tendency to explode unless it is kept refrigerated. The electrolyte used by Gross, methanol-perchloric, is not quite so dangerous. The chemical polishing technique is certainly satisfactory in that it is simple, speedy, reproducible, and versatile. The method used will be determined by the tastes of the particular metallographer. All of the above-mentioned methods are capable of producing good results.

7.5 CORROSION OF HAFNIUM

By J. N. Chirigos⁵

One of the attributes of hafnium which makes it a satisfactory control rod material in pressurized water reactors is its excellent corrosion resistance. It is this property that is the subject of this section, and it will be seen below that the corrosion resistance of hafnium in pressurized water is superior to that of zirconium. Because of the marked similarity between hafnium and zirconium, and since relatively little complete information concerning the corrosion behavior of hafnium is known, every opportunity has been made to compare the properties of hafnium with those of zirconium. The material to be covered will consist of discussion of the corrosion behavior of hafnium in high temperature, high pressure water, chemical reagents, and high temperature dry gases.

Hot Water Corrosion

Most of the results to be discussed were obtained from arc melted crystal bar hafnium containing 2-5 w/o zirconium. Hafnium has not yet been subjected to a systematic study with respect to corrosion kinetics and mechanism in hot water. There are numerous engineering data, however, relating to the corrosion resistance in water and steam [65]. The corrosion resistance of hafnium is evidently far greater than is actually needed in practice. There has, therefore, been no great practical need for detailed study of its corrosion behavior. Corrosion data carrying statistical weight are just becoming available.

Sample Preparation

It has been established that it is necessary to bright etch the surface of hafnium samples to secure reproducible corrosion test results. The pickling solution described here produces a bright surface amounting essentially to a metallographic finish. Prior to the pickling operation, the specimen may be prepared by machining, grinding, or abrading to a finish at least as fine as 63 μ in. rms. The specimens are degreased immediately before pickling. One to two mils of metal are then removed from each surface by pickling in a solution composed of 38 ± 3 cc of 70 percent HNO_3 , 4 ± 1 cc of 48 percent HF , and sufficient water to make 100 cc of solution. For best results, the temperature of the solution should be between 125 and 140° F.⁶ Adequate ventilation to remove the poisonous nitrous

⁵ Westinghouse Atomic Power Division.

⁶ The pickling rate of a freshly prepared solution of 38 parts HNO_3 , 5 parts HF , and 57 parts water at a temperature of 130° F with a volume ratio of 200 parts of solution to one of metal will correspond to approximately one mil of metal removal per minute of immersion.

oxide fumes should be provided during the pickling operation. An important step of the pickling operation is rinsing to remove acid residues from the specimens to prevent staining which will result in a mottled gray film during corrosion testing. Samples removed from the pickling solution should be immediately immersed in cold running tap water and agitated approximately one minute without breaking the surface of the water. Specimens should be allowed to remain in rinse water for five minutes without touching the sides or bottom of the container or resting against other specimens. Material should be then placed in a grade "A"⁷ water bath for a sufficient time to remove all acid residues from the surfaces of the specimens. The criterion for a properly prepared surface is a bright specular appearance with no stains or blemishes. After pickling and rinsing, the samples should be carefully dried using soft lint-free cloths or tissue. If further degreasing or cleaning is necessary, wiping with 180-proof ethanol is recommended.

A hafnium surface which has not been pickled will, after corrosion testing, have a hazy grey appearance and slightly higher weight gain than a pickled specimen. Pickling will also help to detect tungsten and other inclusion-type defects which might go unnoticed on an unpickled surface, since the pickling rate of these particles is different from that of hafnium.

Experimental Data

In some instances, reported values for corrosion rates are based upon results obtained from one sample and, consequently, the reproducibility of the data is unknown. In others, the data are based on averages of at least 25 samples. These data indicate that, upon exposure to water, hafnium forms a protective oxide film that grows very slowly with time. For example, in 600° F water at 1,500 psi, the weight increase of 5.5 mg/dm² that is experienced after 74 days rises to only 6.0 mg/dm² after a total time of 253 days. In 680° F water at 2,700 psi, a weight gain of 6–9 mg/dm² is attained after 44 days and essentially remains at this value up to about 200 days. In 1,500-psi, 750° F steam, a gradual weight increase is observed which can be expressed empirically as

$$W = Kt^{0.59},$$

where

K lies in the range 0.32 to 0.76 mg/dm²—days^{0.59},

W is in mg/dm²,

and

t is the test time in days.

⁷ Grade "A" water is defined as distilled and/or deionized water having a pH of between 6 and 8 and a specific resistivity of at least 5×10^5 ohm-cm.

It is interesting to observe that for times in excess of 70 days in 750° F steam, the corrosion product is a film that still exhibits interference colors.

Table 7.28 summarizes the corrosion behavior of crystal bar hafnium in hot water and steam. The appropriate data for Zircaloy-2 are entered for comparison.

TABLE 7.28—CORROSION IN WATER AND STEAM, APPROXIMATE WEIGHT INCREASE IN mg/dm² AT INDICATED TEMPERATURE

| Time (days) | 600° F water saturation pressure | | 680° F water saturation pressure | | 750° F steam (1,500 psi) | |
|-------------|----------------------------------|------------|----------------------------------|------------|--------------------------|------------|
| | Hf | Zircaloy-2 | Hf | Zircaloy-2 | Hf | Zircaloy-2 |
| 44----- | 5 | 14 | 6-9.0 | 27 | 4-7 | 48 |
| 195----- | 6 | 21 | 7-9.0 | 65 | 7 | 210 |
| 294----- | (¹) | 23 | (¹) | 100 | 9 | 300 |

¹ Data not available.

Table 7.28 indicates very clearly that the corrosion properties of hafnium in hot water are very superior to those of Zircaloy-2. It is to be emphasized that the weight change data for hafnium in this table are to be considered only as rough indications of corrosion behavior, since the reproducibility is probably no better than 50 percent. All data examined indicate higher weight gains in 680° F water at saturation pressure than in 750° F steam at 1,500 psi for short-time tests (usually less than 100 days). The reasons for this behavior are unknown.

A systematic study of the corrosion behavior of hafnium and associated hydrogen pickup has been initiated by F. A. Nichols [66]. Partial data indicate that degassed material (15 mil foil) with a pre-corrosion hydrogen content of approximately 5 ppm does not suffer any significant hydrogen pickup after 84 days test in 600 and 680° F water at saturation pressure and 750° F steam at 1,500 psi. Preliminary X-ray analysis of the corrosion product in situ revealed monoclinic HfO₂. Furthermore, the intensities of lines obtained by this technique relative to intensities observed on powder photograms indicate a (001) texture in the oxide. The texture in the rolled metal sheet was (0001). The partial orientation relationship observed here for Hf/HfO₂ is not the same as that observed for Zr/ZrO₂. In zirconium, the observed relationship was (011) texture in the oxide parallel to (0001) texture in the metal [67]. This point deserves further investigation.

The corrosion resistance of crystal bar zirconium is extremely sensitive to level of impurities and condition of surface prior to corrosion. From what little evidence there is, it appears that hafnium may be superior to crystal bar zirconium and Zircaloy-2 in both respects. For example, hafnium sections can be joined by welding in air, and, if they are then properly pickled, there is no apparent loss in corrosion resistance [16]. Zirconium or Zircaloy on the other hand (following such a treatment) would pick up sufficient nitrogen to greatly impair corrosion resistance. The specific effect of nitrogen contamination on hafnium corrosion can be seen in Table 7.29. Data for Zircaloy-2 are entered for comparison.

TABLE 7.29—THE EFFECT OF NITROGEN ON THE CORROSION RESISTANCE OF HAFNIUM IN WATER AND STEAM [68]

| Nitrogen content (ppm) | Weight gain in 680° F water (mg/dm ²) | | Weight gain in 750° F steam (mg/dm ²) | | | |
|------------------------|---|----------|---|----------|----------|----------|
| | 252 days | 280 days | 95 days | 102 days | 109 days | 116 days |
| 500----- | 15 | 23 | 22 | 23 | 22 | 24 |
| 750----- | 35 | 48 | 36 | 37 | 37 | 37 |
| 1000----- | 83 | 94 | 66 | 70 | 70 | 75 |
| Zircaloy-2----- | 83 | 100 | 87 | 91 | 90 | 110 |

The results in Table 7.29 obtained by Kato and Carver [68] at the Bureau of Mines, Albany, Oreg., have been interpreted by these investigators to mean that the nitrogen tolerance of hafnium is 1,000 ppm, because at this level of nitrogen, the weight gain per unit area of oxygen pickup by hafnium is equivalent to that of Zircaloy-2 under similar conditions. This is not necessarily the only interpretation of these observations. The actual nitrogen tolerance of hafnium, however, defined in a way similar to that for zirconium and Zircaloy-2 [31], is that nitrogen level above which the rate of corrosion exceeds the normal rate. To determine such a tolerance, it is necessary to plot weight change data versus nitrogen content for the several time periods involved and then, from a careful examination of the curve, to choose that nitrogen content beyond which the weight gain rises significantly above the normal level. Such curves have been plotted from the data of Carver and Kato and are presented in Figures 7.35 and 7.36. The points at 50 ppm nitrogen represent arc-melted hafnium crystal bar suitable for use in nuclear reactors.

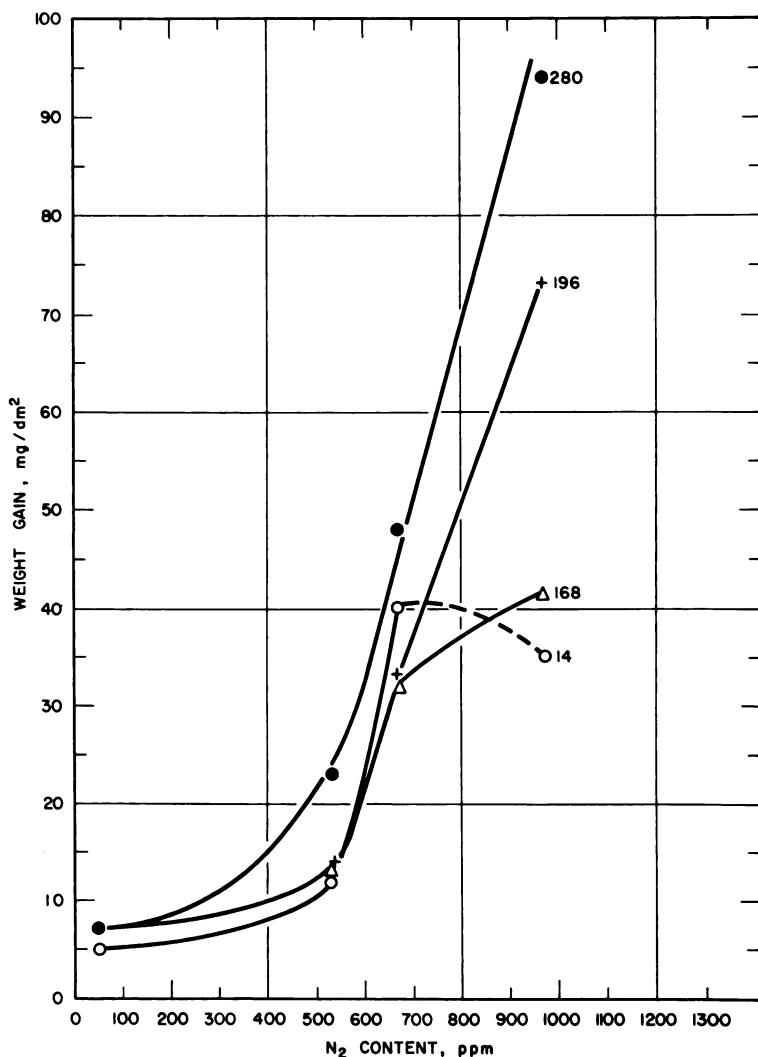


FIGURE 7.35. Weight Gain vs. Nitrogen Content for Hafnium in 680° F Water at Saturation Pressure. Numbers on Curves Refer to Exposure Time in Days.

These curves indicate that, on an absolute basis, the nitrogen tolerance is well below 1,000 ppm and very likely below 500 ppm. Unfortunately, the lack of data between 50 and 500 ppm makes it impossible, at this time, to state conclusively the nitrogen tolerance. It does appear, however, that the nitrogen tolerance, based on the long-time curves at either 750° or 680° F, is less than 500 ppm, perhaps at 200–250 ppm. In zirconium (unalloyed) the tolerance for nitrogen is about 50 ppm. As the nitrogen level increases, zirconium corrodes more rapidly until, at approximately 100 ppm, disintegration occurs. If the nitrogen tolerances of the two metals are

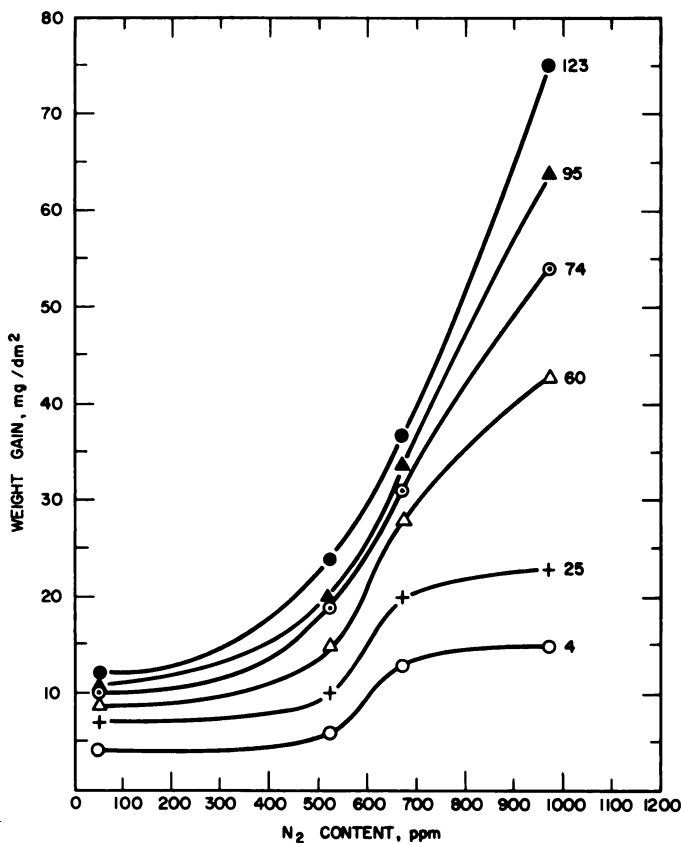


FIGURE 7.36. Weight Gain vs. Nitrogen Content for Hafnium in 750° F Steam at 1,500 psi. Numbers on Curves Refer to Exposure Time in Days.

expressed in atomic percent, it is still evident that hafnium can accommodate more nitrogen than zirconium from the standpoint of corrosion resistance.

Effect of Alloy Additions

Because the properties of commercial hafnium have been adequate for direct nuclear application, little information is available on the corrosion of most of its alloys. Nevertheless, the work of Carver and Hayes [69] offers a fairly complete picture of the corrosion behavior of hafnium-titanium alloys. In this study, alloys of titanium in hafnium were made by the addition of 10 w/o increments of titanium. The alloy buttons were arc melted and hot rolled to 0.150-inch thick sheet. Specimens were given a 900° C, 48-hour vacuum anneal prior to corrosion. Unfortunately, this study did not include unalloyed hafnium, and, consequently, direct comparison of the effect of titanium cannot be made. The authors did incorporate a Zircaloy-2

standard during corrosion testing. The weight change versus time data for 680° F water and 750° F steam are to be seen in Figures 7.37 and 7.38. The effect of titanium concentration can better be seen in Figure 7.39, wherein is plotted the weight gain after 14 days in 680° F water versus percent titanium. The datum of zero percent titanium is taken from the work of Nichols. This plot indicates a minimum in corrosion resistance occurring at <10 w/o titanium in hafnium. This behavior is to be compared with that of the zirconium-titanium system, wherein a minimum in corrosion resistance is to be found in the range of 0.1 to 4 w/o titanium in zirconium [31].

Effect of Cold Work

Samples of hafnium cold reduced 10 percent and corrosion tested in 680 and 600° F water for 70 days showed weight gains comparable with those observed for nonworked material [70]. Thus, it appears that significant amounts of cold work can be tolerated without harmful consequence.

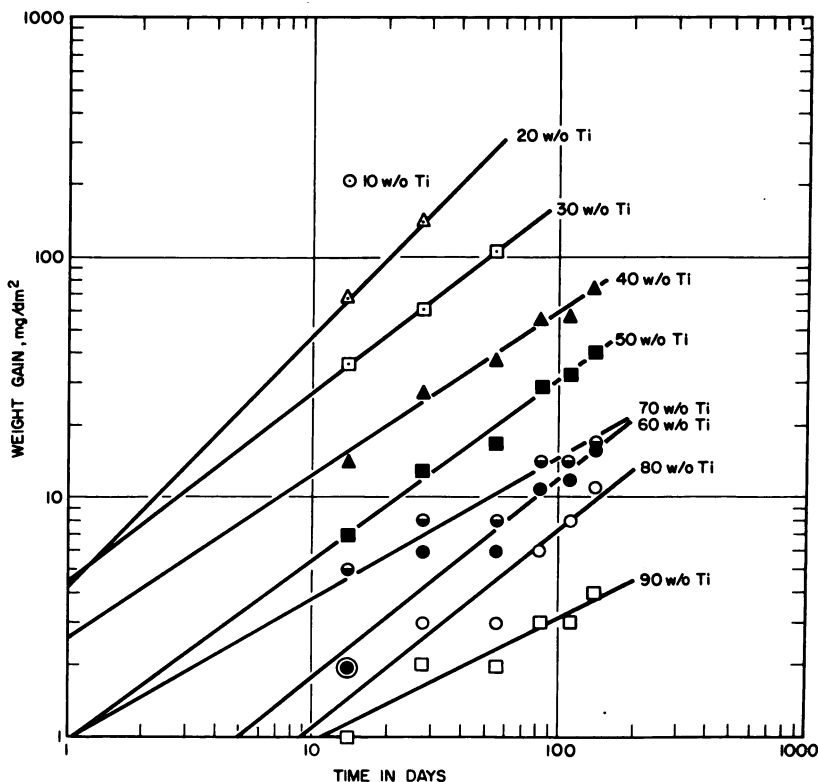


FIGURE 7.37. Corrosion of Hafnium-Titanium Alloys in 680° F Water at Saturation Pressure.

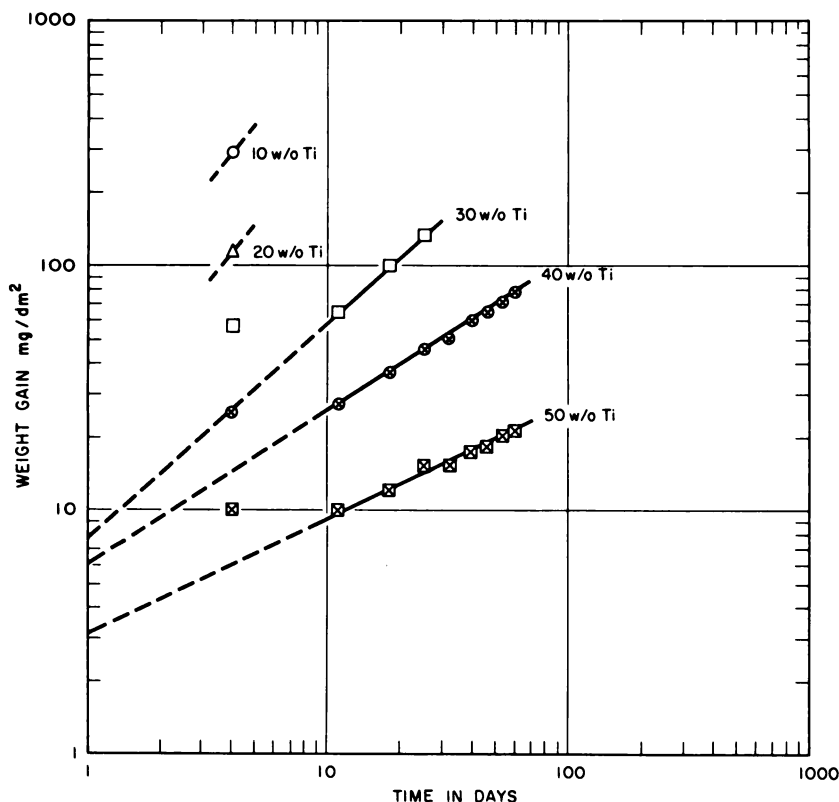


FIGURE 7.38. Corrosion of Hafnium-Titanium Alloys in 750° Steam, 1,500 psi.

Effect of Irradiation

A limited amount of data indicates that the corrosion resistance of hafnium is not adversely affected by exposure to irradiation. Samples tested for 6 months in 540° F water under 1×10^{20} nvt slow and 1×10^{19} nvt fast integrated neutron fluxes exhibited weight changes of 7–8 mg/dm²/mo [71]. In addition, hafnium metal has seen extensive use as a control rod material in operating nuclear reactors without indications of excessive corrosion under irradiation.

The above discussion clearly demonstrates the suitability of hafnium as a reactor material: good corrosion resistance, essentially unaffected by small amounts of cold work and contamination. Reliable kinetic data have not been obtained, nor is anything known about the mechanism of water corrosion. Until such data are obtained, one must rely solely on the behavior of zirconium as a guide.

Nucleate Boiling

The effect of nucleate boiling on the corrosion behavior of hafnium in flowing high temperature water was studied by Esper [72].

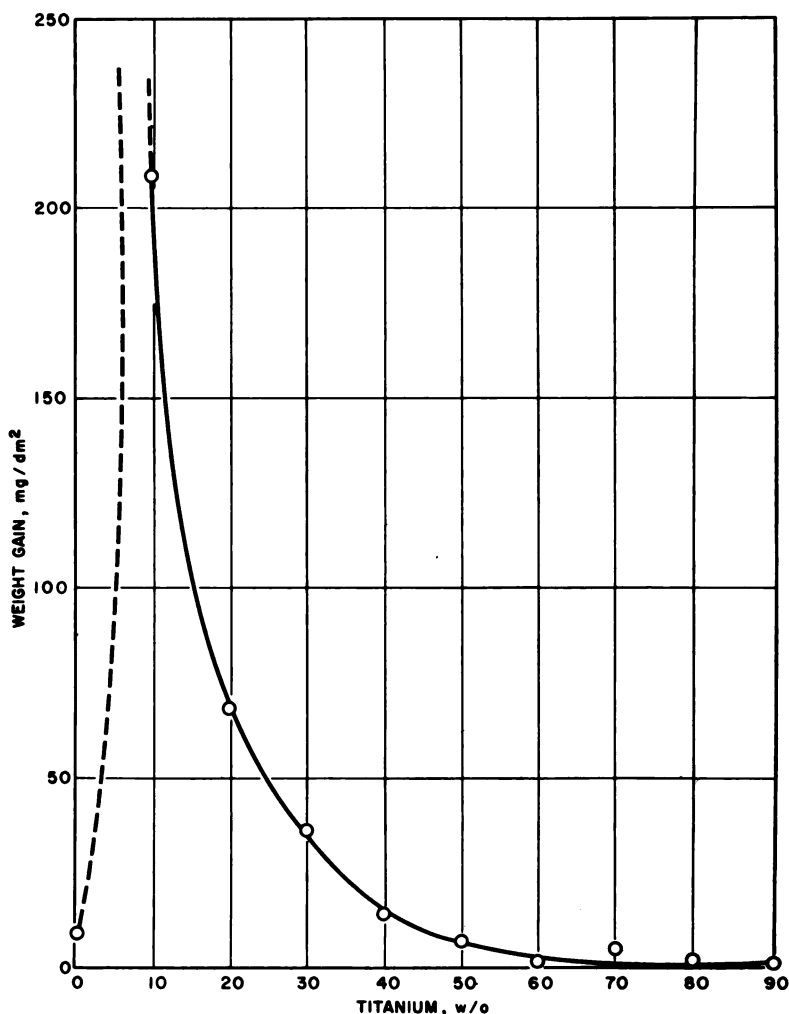


FIGURE 7.39. Weight Gain vs. Titanium Concentration in Hafnium-Titanium Alloys after 14 Days in 680° F Water at Saturation Temperature.

Tubular specimens of reactor grade hafnium, previously bright etched in an aqueous nitric-hydrofluoric acid solution, were exposed to water under the conditions shown in Table 7.30. Heat fluxes and flow velocities were adjusted so that some specimens were exposed under forced convection in a nonboiling condition, whereas others were permitted to undergo nucleate boiling. After exposure for 1,044 hours only a lustrous temper film of corrosion product oxide was evident on the two types of specimens.

TABLE 7.30—SUMMARY OF TEST CONDITIONS FOR STUDYING THE EFFECT OF NUCLEATE BOILING ON CORROSION OF HAFNIUM IN DYNAMIC WATER [72]

| <i>Test Conditions</i> | |
|--|---------------|
| Test duration (hr)..... | 1,044 |
| Heat flux (Btu/hr-ft ²)..... | 300,000 |
| Pressure (psi)..... | 2,000 ± 50 |
| Velocity (fps)..... | 4-5 |
| Nonboiling specimen inlet water temperature (° F)..... | 510 |
| <i>ΔT=125° F</i> | |
| Nonboiling specimen, outside wall temperature (° F)..... | 635 |
| Boiling specimen, inlet water temperature (° F)..... | 585 |
| <i>ΔT=75° F</i> | |
| Boiling specimen, outside wall temperature (° F)..... | 660 |
| pH..... | 10-11 |
| Resistivity (ohm-cm)..... | 20,000-50,000 |
| H ₂ concentration (cc/kg)..... | 20-30 |
| O ₂ concentration (cc/kg)..... | 0.1 |

Metallographic examination of sections taken perpendicular to the surfaces indicated that the thickness of the oxide film was 2×10^{-5} inches both in the case of the boiling and nonboiling specimens. Thus, nucleate boiling under those conditions does not result in any measurable increase of corrosion rate. Hydrogen analyses were made to determine the extent of hydrogen pickup, but the results were too scattered to permit a conclusion to be drawn.

High Temperature Gas-Metal Reactions

Air

The first observations made indicated that hafnium had excellent resistance to attack by air at elevated temperatures. For example, hafnium oxidizes in air at about the same rate as zirconium at 1,380° F, but at one-half the rate of zirconium at 1,650° F. The metal can be hot worked at 1,650° F without protection [73]. No systematic study has been performed. If the behavior of zirconium can be taken as a guide, the relatively low reaction rates of hafnium with oxygen and nitrogen are not likely to be maintained in oxygen-nitrogen mixtures.

Oxygen

The only systematic study made thus far of the reaction kinetics of hafnium with pure, dry oxygen is that of Smeltzer and Simnad [74]. It is to be emphasized that the hafnium crystal bar material

used contained about 5.0 w/o Zr. The measurements were made at oxygen pressures of 760 mm of Hg and covered the temperature range of 350–1,200° C. The course of the reaction was followed gravimetrically. A microbalance was used in the temperature range 350–800° C, while a helical spring balance was used in making measurements in the range 800–1,200° C. The data were found to successively follow logarithmic, parabolic, and linear rate laws, with activation energies of 11.4, 36.0, and 26.1 kcal, respectively.

The following appropriate logarithmic, parabolic, and linear rate equations were found to represent the data:

$$\left(\frac{\Delta M}{A}\right) = 2 \times 10^{-2} \left(\exp - \frac{11,400}{RT} \right) \ln \left[1 + \left(7.7 \exp - \frac{5400}{RT} \right) t \right],$$

$$\left(\frac{\Delta M}{A}\right)^2 = \left(6 \times 10^{-2} \exp - \frac{36,000}{RT} \right) t + a(T),$$

and

$$\left(\frac{\Delta M}{A}\right) = \left(6 \times 10^{-2} \exp - \frac{26,100}{RT} \right) t + b(T).$$

Here, $\frac{\Delta M}{A}$ is the gram quantity of oxygen reacted per square centimeter, t is the time in minutes, R and T retain their usual meaning, and a and b are temperature dependent constants. Typical reaction curves illustrating the three types of oxidation are to be found in Figures 7.40, 7.41, and 7.42. Figures 7.40 and 7.41 also illustrate the

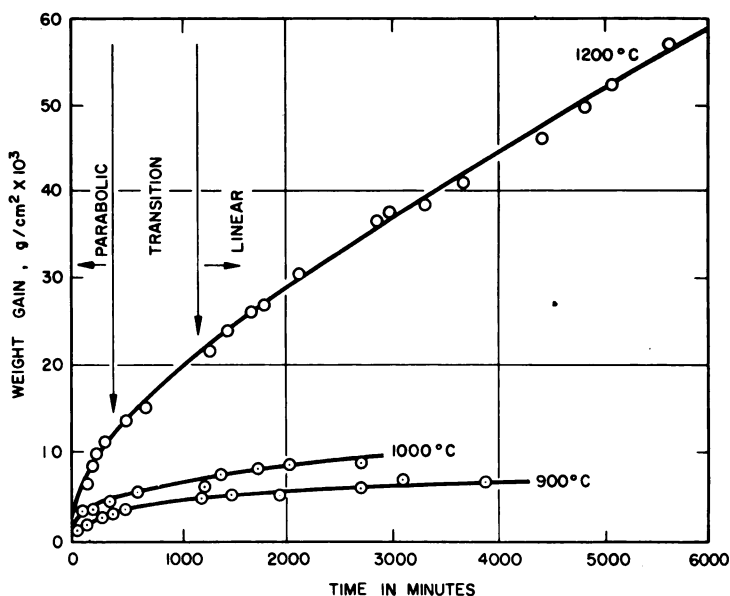


FIGURE 7.40. Hafnium Oxidation in the Temperature Range 900 to 1,200° C; Data Plotted According to a Linear Equation.

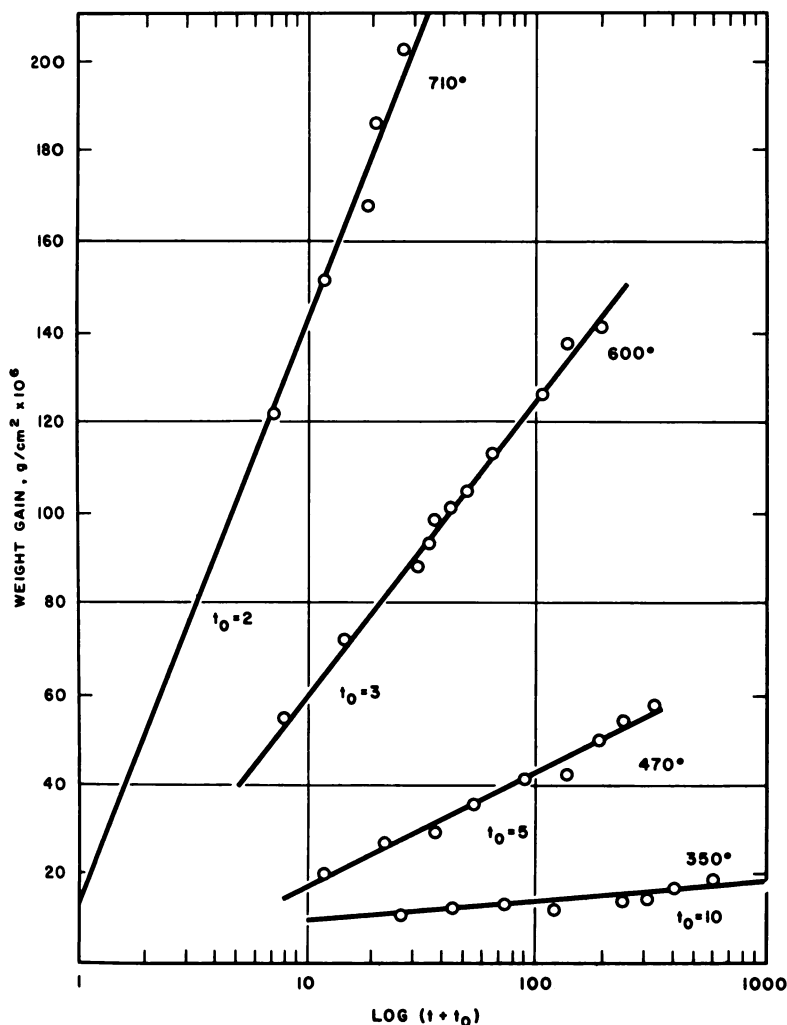


FIGURE 7.41. Hafnium Oxidation in the Temperature Range 350 to 710° C; Data Plotted According to a Logarithmic Equation.

significance of the temperature dependent constants, a and b . Figures 7.43 and 7.44 show the Arrhenius plots for the observed rate laws. The parabolic rate constant was found to be independent of pressure over the range 10–760 mm. The logarithmic and parabolic laws are correlated with the formation of compact oxides, while the linear rate law is accounted for by a porous scale. The maximum thickness of compact oxide in duplex scales was found to be described by the following reaction:

$$\left(\frac{\Delta M}{A}\right)_{\max} = 5 \times 10^{-1} \exp \frac{9,900}{RT}.$$

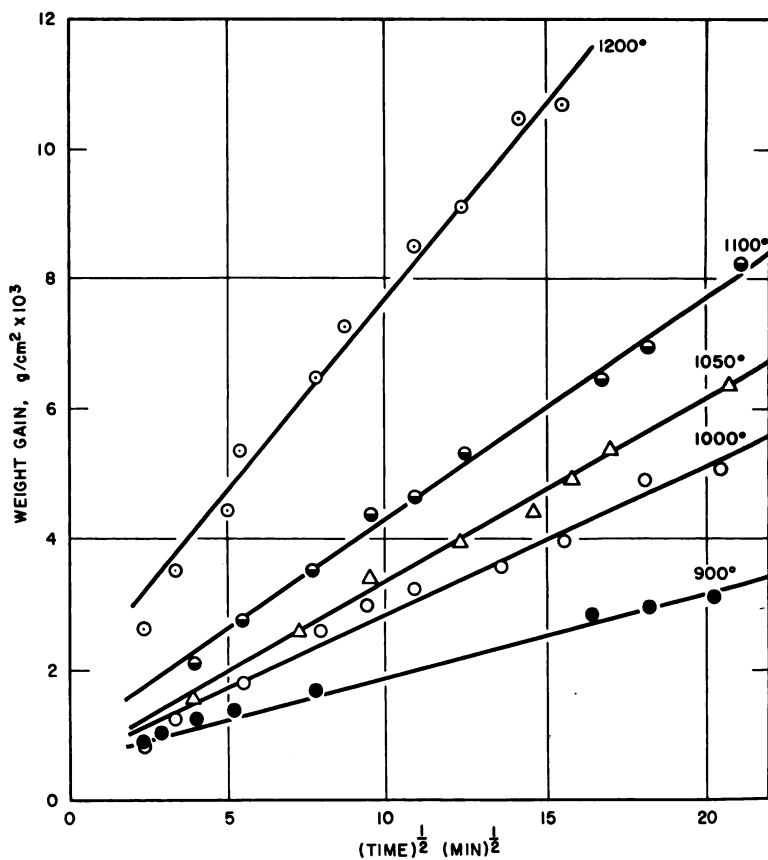


FIGURE 7.42. Hafnium Oxidation in the Temperature Range 900 to 1200° C; Data Plotted According to a Parabolic Equation.

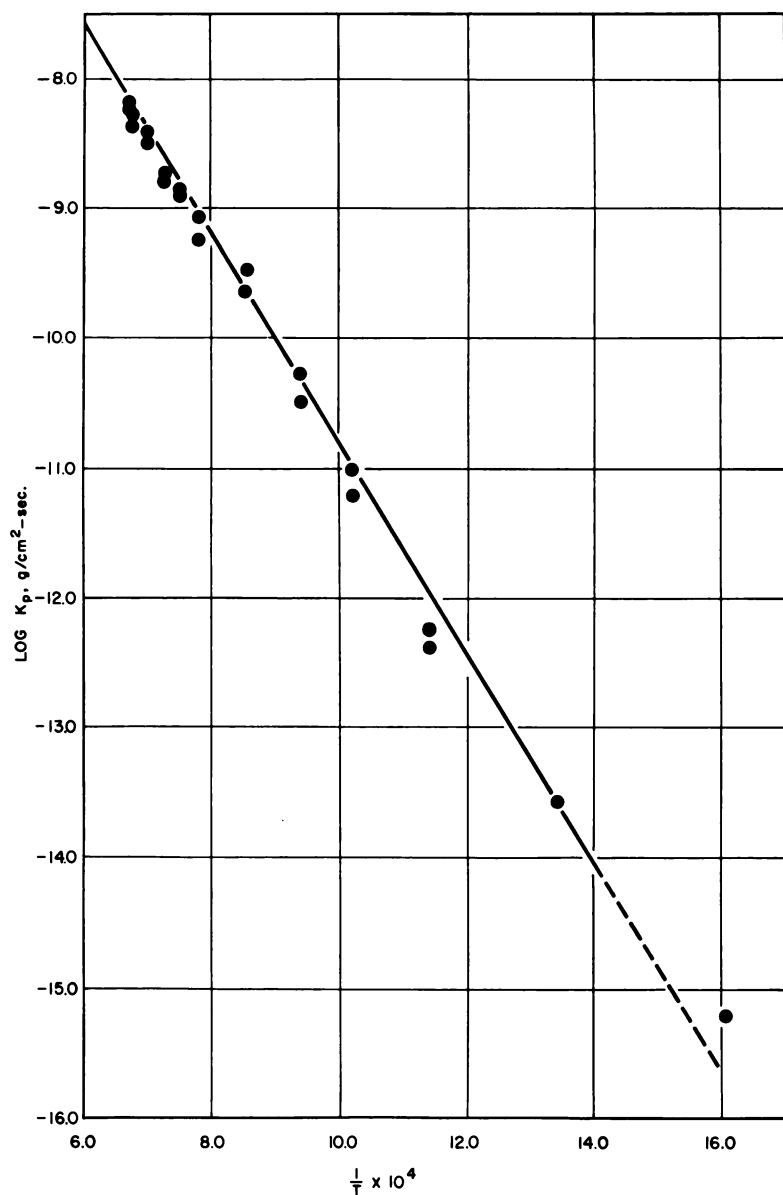


FIGURE 7.43. Arrhenius Plot of Parabolic Rate Constants in the Temperature Range 350 to 1,200° C.

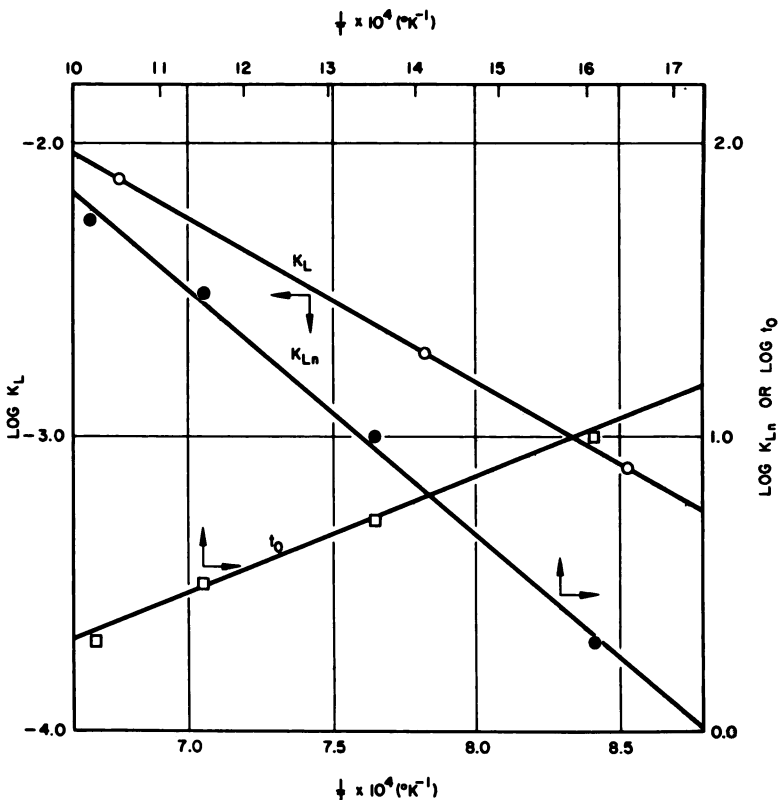


FIGURE 7.44. Arrhenius Plot of Linear and Logarithmic Rate Constants for the Oxidation of Hafnium in Oxygen.

Smeltzer and Simnad analyzed their empirical oxidation data by correlation with the accepted "laws" of oxidation; logarithmic, parabolic, and linear. It is interesting to observe that an equally good correlation can be obtained by assuming the validity of a generalized "parabolic" rate law expressed as

$$\Delta W = (kt)^n,$$

where

ΔW = weight gain per unit area (mg/dm^2),

t = time (min),

k = "rate" constant,

and

n = reaction index.

The oxidation data are represented in a plot of $\log \Delta W$ versus $\log t$ in Figure 7.45, and the values of n and k calculated from these curves appear in Table 7.31. Figure 7.46 is a plot of $\log k$ versus $\frac{1}{T}$ and

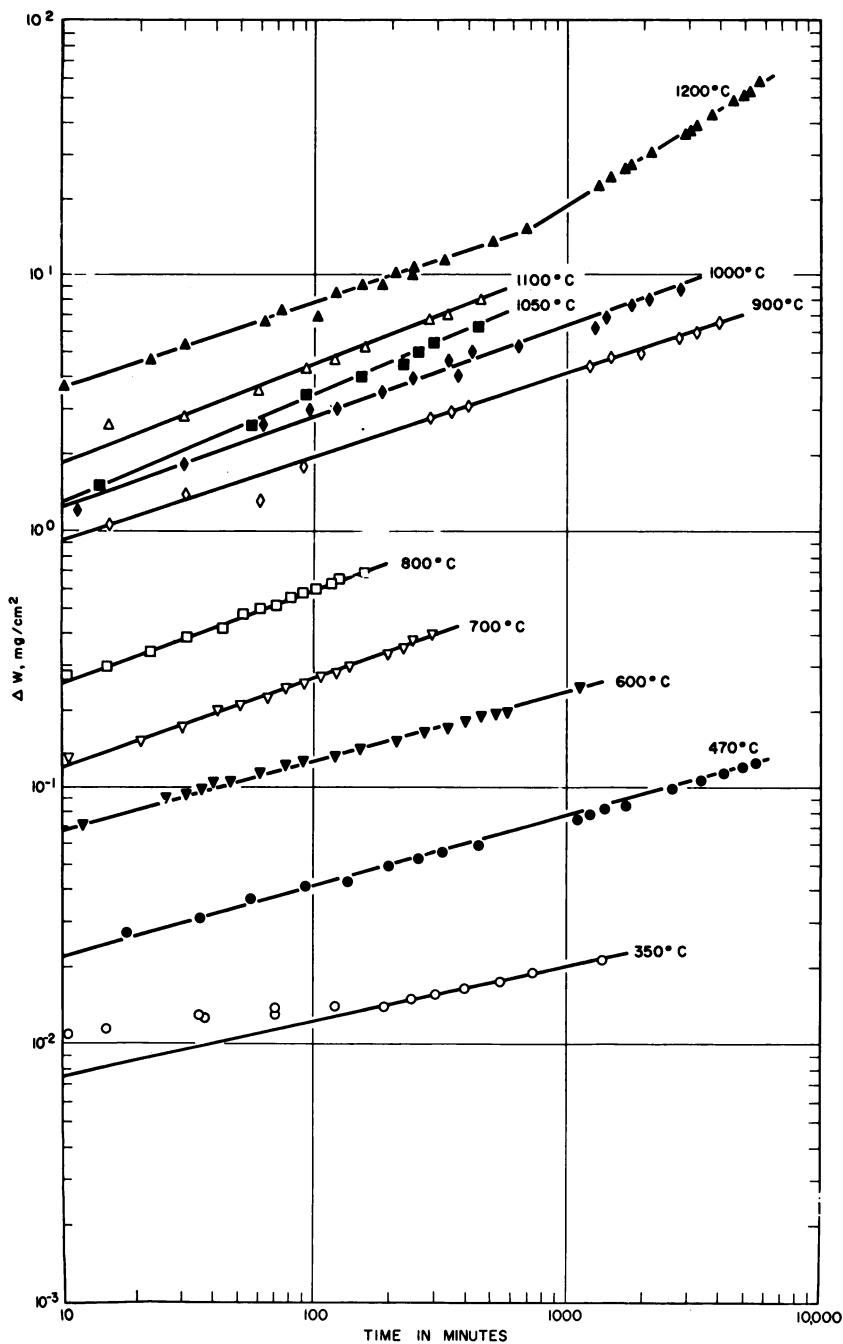


FIGURE 7.45. Log-Log Plot of Smeltzer's and Sinnad's Hafnium Oxidation Data ; Generalized "Parabolic" Rate Law.

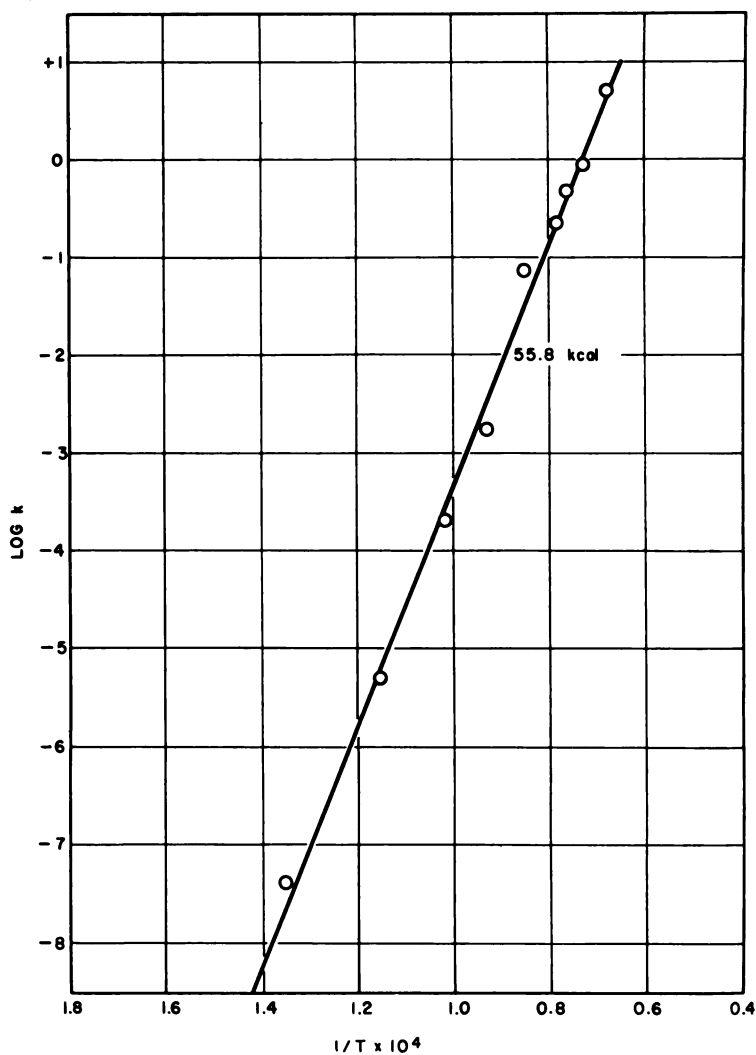


FIGURE 7.46. Arrhenius Plot of Data from figure 7.45.

yields an activation energy of 56 kcal. Thus, it can be seen that all data, with the exception of the initial portion of the 350° C and the latter portion of the 1,200° C curves, can be correlated.

TABLE 7.31—VALUES OF k AND n CALCULATED FROM THE RELATIONSHIP $\Delta W = (kt)^n$

| Temperature (° C) | k | n |
|-------------------|------------------------|-------|
| 350..... | 1.82×10^{-11} | 0. 22 |
| 470..... | 1.74×10^{-8} | 0. 27 |
| 600..... | 5.0×10^{-6} | 0. 27 |
| 710..... | 2.1×10^{-4} | 0. 35 |
| 800..... | 1.78×10^{-3} | 0. 31 |
| 900..... | 7.3×10^{-2} | 0. 32 |
| 1000..... | 2.2×10^{-1} | 0. 35 |
| 1050..... | 1.1×10^{-1} | 0. 43 |
| 1100..... | 6.98×10^{-1} | 0. 36 |
| 1200..... | 4. 9 | 0. 34 |

Recent work by Pemsler [75] on the diffusion of oxygen into hafnium was conducted by measuring the disappearance of interference colors due to the buildup of thin hafnia films on hafnium while heating to elevated temperatures. The results of these experiments give a value of about 52 kcal for the activation energy of diffusion of oxygen into hafnium. This figure compares favorably with the value of 56 kcal calculated for the oxidation of hafnium from the data of Smeltzer and Simnad. For the oxidation of zirconium and diffusion of oxygen into zirconium, the corresponding activation energies are approximately 48 and 52 kcal [76]. Thus, treatment of the oxidation data according to the "generalized parabolic" rate law reveals a possible correspondence between the over-all oxidation reaction and the diffusion of oxygen into the metal for both hafnium and zirconium. The rate of oxygen penetration into the metals titanium, zirconium, and hafnium and its relation to loss of protective-type oxidation toward "break-away" or "transition" is discussed in a recent paper by Wallwork and Jenkins [77]. These latter authors performed a metallographic study on the oxide-metal interface region of oxidized titanium samples. By means of hardness penetration curves, the existence of a fixed zone of oxygen penetration in titanium metal was demonstrated. Wallwork and Jenkins propose that the establishment of this zone is to be associated with "parabolic" oxidation, whereas linear oxidation occurs subsequent to establishment of the oxygen penetration zone.

Smeltzer and Simnad, who treated their data according to the log-log plot, however, did not extend the analysis toward calculation of

"activation" energies based upon log-log representations of their data. Many investigators disagree as to the exact form in which ΔW is to be expressed—e.g., $\Delta W = Kt^n$ or $(kt)^n$ [78, 79]. In addition, the question arises as to the physical meaning to be attached to an "activation" energy obtained from Arrhenius-type plots involving K or k , which are related by $K = k^n$. Nevertheless, it is emphasized that here an adequate empirical description of the data of Smeltzer and Simnad can be obtained, and the "activation" energy so deduced is substantiated somewhat by the work of Pemsler and the analogous picture obtained for the oxidation of zirconium [76].

Diffusion of Oxygen in Hafnium

The results of Pemsler [75], mentioned above in relation to the oxidation of hafnium, were obtained over the temperature range of 500–620° C. This study, as indicated, was directed toward measurement of the diffusion coefficient of oxygen in hafnium and was effected by measuring the rate of dissolution of oxide films into the metal in vacuo. The films were formed electrolytically, and the factor relating film thickness to applied voltage was 18.9 Å/volt. To calculate diffusion coefficients, Pemsler had to assume values for the density of oxygen-saturated metal, the density of monoclinic hafnia, and the solubility of oxygen in hafnium. The density of 10.22 g/cc, Table 7.32, was taken for monoclinic hafnia. The value of density for the oxygen saturated metal was taken arbitrarily as 13.5 g/cc. No data for the solubility of oxygen in hafnium are known, and the diffusion coefficients were calculated for three assumed values of oxygen saturation—20, 30, and 40 a/o. The intermediate value corresponds to the saturation concentration of oxygen in zirconium. Accordingly, the diffusion constants are expressed as

$D = 1.4 \exp(-51,800/RT)$ for solubility of 20 a/o oxygen,

$D = 0.47 \exp(-51,800/RT)$ for solubility of 30 a/o oxygen,
and

$D = 0.14 \exp(-51,800/RT)$ for solubility of 40 a/o oxygen.

Over-estimation of the solubility limit of oxygen in hafnium will tend to make the calculated D values less than the true value.

In all studies made to date, the only observed product of the reaction of hafnium with oxygen has been monoclinic, HfO_2 , hafnia. Curtis, Doney, and Johnson [80] have made a thorough study of the properties of hafnium oxide, and many of their results are to be

found in Table 7.32. Data pertaining to zirconia are entered for comparison.

TABLE 7.32—PROPERTIES AND CRYSTALLOGRAPHIC DATA FOR HAFNIA AND ZIRCONIA [80]¹

A. PROPERTIES

| Property | HfO ₂ | ZrO ₂ |
|-------------------------------|--|--|
| Heat of formation | 266.1 ± 0.3 kcal..... | 257.4 ± 0.6 kcal [81]. |
| Melting point | 2,900° C. ± 25° C..... | 2,850° C. ± 25° C. |
| Index of refraction | 1.98–2.02..... | 2.1–2.2. |
| Linear expansion coefficient. | 5.8 × 10 ⁻⁶ in./in./C° (monoclinic). | 8.0 × 10 ⁻⁶ in./in./C° (monoclinic). |
| Theoretical density | 10.22 g/cc (monoclinic) .. | 5.68 g/cc (monoclinic). |
| | 10.06 g/cc (tetragonal) .. | 6.10 g/cc (tetragonal). |
| Pycnometer density | 9.68 g/cc (monoclinic). | |

B. CRYSTALLOGRAPHIC DATA

| Modification—Range of stability | HfO ₂ | | | ZrO ₂ | |
|---------------------------------|---|-----------------|----------------------|---|---------------------|
| | Monoclinic—Room temperature to 1,700° C | | Tetragonal—1,700° C+ | Monoclinic—Room temperature to 1,000° C | Tetragonal—1,000° C |
| | <i>R. T.</i> | <i>1,640° C</i> | <i>1,920° C</i> | <i>R. T.</i> | <i>>1,000° C</i> |
| <i>a</i> ₀ | 5.11 Å | 5.21 Å | 5.14 Å | 5.21 Å | 5.07 Å |
| <i>b</i> ₀ | 5.14 Å | 5.15 Å | ----- | 5.26 Å | ----- |
| <i>c</i> ₀ | 5.28 Å | 5.43 Å | 5.25 Å | 5.375 Å | 5.16 Å |
| <i>β</i> | 99° 44' | 98° 48' | ----- | 99° 58' | ----- |

¹ Courtesy of the American Ceramic Society.

Nitrogen

Edwards and Malloy [82] have measured the reaction kinetics of hafnium (2.5 w/o zirconium) with nitrogen by a volumetric technique. The measurement encompassed the temperature range 876–1,034° C and pressure range of 38–402 mm of mercury. Their data were described by the parabolic rate law and yielded an activation energy of about 57 kcal/mol. The kinetics were essentially independent of pressure over the range studied. X-ray analysis of the golden-yellow reaction product indicated face centered cubic hafnium nitride of lattice parameter 4.50 Å and theoretical density 14.0 g/cc. Comparison of the data with those for titanium and zirconium shows that the reaction rates decrease in the order titanium, zirconium, and hafnium.

Hydrogen

There are scattered pieces of information which indicate that the reaction kinetics of hafnium with hydrogen are very similar to those of zirconium. Waldo and Anderson [83] found that the maximum uptake of hydrogen at one atmosphere pressure occurred at 700° C. Hydrogen could readily be removed from the metal by heating at 900° C in a vacuum of about 10^{-5} mm Hg. What is known of the hafnium-hydrogen phase relations is discussed in detail in Chapter 6.

Corrosion Behavior in Miscellaneous Media

There is a limited amount of information available pertaining to the corrosion behavior of hafnium in various chemical media. Table 7.33, taken from Everhart [73], permits a direct comparison to be made of the corrosion rates of hafnium, zirconium, and titanium in many inorganic solutions. The data represent results obtained by allowing metal platelets to react with the solution at 35° C for two weeks.

From Table 7.33 it can be concluded that the corrosion resistance of hafnium in acids is slightly inferior to that of zirconium. It appears that, in corrosion in mineral acids, hafnium resembles titanium more than it does zirconium.

A limited amount of data indicates that hafnium is as resistant to 500° C sodium as is stainless steel, the corrosion rate being approximately 0.1 mg/cm²/mo [84].

TABLE 7.33—CORROSION RATE IN VARIOUS MEDIA, INCHES PER YEAR [73]¹

Temperature = 35°C

Time = 2 weeks

| Corrosion medium | Hf | Zr | Ti |
|--|-----------------------|-----------------------|-------------------------|
| H ₂ SO ₄ (96.2%) | Soluble | Soluble | 0.17. |
| H ₂ SO ₄ (10%) | 3.5×10^{-4} | 0.36×10^{-4} | 3.2×10^{-4} . |
| HCl (37%) | 13×10^{-4} | 6.1×10^{-4} | Soluble. |
| HCl (10%) | 3.5×10^{-4} | 0.12×10^{-4} | 2.5×10^{-4} . |
| HNO ₃ (fuming) | 4.4×10^{-4} | Gains wt. | Gains wt. |
| HNO ₃ (69.7%) | 1.8×10^{-4} | Gains wt. | 8.64×10^{-4} . |
| HNO ₃ (10%) | 3.5×10^{-4} | 0.12×10^{-4} | 1.2×10^{-4} . |
| HCl-HNO ₃ (1:1) | 0.13 | Slowly attacked | 3.9×10^{-4} . |
| HCl-H ₂ SO ₄ (1:1) | 4.8×10^{-4} | 0.79×10^{-4} | Soluble. |
| HNO ₃ -H ₂ SO ₄ (1:1) | 0.19 | 0.0865 | 48×10^{-4} . |
| NaOH (50%) | 1.8×10^{-4} | Gains wt. | 3.5×10^{-4} . |
| NaCl (20%) | 0.88×10^{-4} | 0.24×10^{-4} | 0.18×10^{-4} . |

¹ Courtesy of Materials and Methods.

Straumanis and Ballass [85] made a study of the rate of dissolution of hafnium in acids, particularly hydrofluoric. It was found that the only other acid that significantly attacked hafnium was aqua regia. In general, hafnium, like zirconium, was found to dissolve as a quadrivalent ion. Normally, additions of fluoride ion to otherwise inert acids speed up the rate of solution of hafnium. A notable exception is iodic acid.

Anodizing Experiments

Additional information pertaining to the oxidation of hafnium can be drawn from the anodizing experiments of Misch and Ruth [86] and Misch and Fisher [87]. These authors demonstrated that monoclinic HfO_2 films could be grown on hafnium electrolytically. The oxide film growth was found to depend on grain orientation when hafnium was anodized at room temperature. The orientation dependence persisted to 90°C , but at this temperature, preferred sites of nucleation of the film became evident.

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Chapter 8

THE ANALYTICAL CHEMISTRY OF HAFNIUM

By G. W. GOWARD¹ AND R. M. JACOBS¹

8.1 INTRODUCTION

The application, in 1922, of the techniques of X-ray spectroscopy by de Hevesy and Coster to the identification of hafnium in zirconium preparations [1] constituted the first analytical determination of the element. Although the investigations of Urbain tended to place element 72 in the rare-earth group of elements, the Bohr atomic theory definitely indicated that the element should be quadrivalent and, thus, belong to the titanium group of the periodic arrangement. At Bohr's suggestion, Coster and de Hevesy examined the X-ray spectra of zirconium residues from Norwegian and Greenland zircons and found reasonably conclusive evidence of the presence of element 72 in the preparations. Because of equipment limitations in regard to the possible interference of the second-order zirconium K lines and the first-order hafnium L lines, the investigators withheld announcement of the discovery until they had prepared a pure hafnium fraction by fractional crystallization of the potassium and ammonium double fluorides of the two elements. Modifications of the fundamental spectroscopic practices as applied by de Hevesy and Coster remain as the most valuable analytical techniques for the routine analysis of the two elements in the presence of each other.

The extreme similarity of the two elements has presented the analytical chemist with an almost unequalled problem in separation. Prior to the nuclear application of the two elements, nearly all analytical results for zirconium were fully acceptable on the basis that they collectively represented zirconium and hafnium. Although a number of relatively facile methods of separation have been developed in the past twenty years, the methods have not been widely applied in the real sense of analytical separation primarily because of the ease with which the two elements can be determined by spectroscopic techniques.

¹ Westinghouse Atomic Power Division.

A further ramification of the similarity of the two elements is that the analytical chemistry of one cannot be discussed without including that of the other. The slight differences in chemical behavior are negligible for virtually all reactions utilized for the so-called "classical wet methods" of analysis. For these reasons, practically all published analytical information on the element hafnium is to be found in conjunction with that on zirconium. This chapter is no exception to this rule. In describing the analytical chemistry of hafnium, the authors have drawn heavily from the published literature on zirconium. However, considerable emphasis has been placed on methods of separation and determination of the two elements in their mutual presence.

In the atomic energy field the major concern of the metallurgist, insofar as analysis is concerned, is a knowledge of the impurity content of hafnium metal. With the exception of the determination of zirconium as an impurity in the metal, essentially no analytical methods have been published for the analysis of hafnium. It has been the authors' experience that the published chemical methods for the analysis of zirconium for impurities are applicable without modification to the analysis of hafnium. With some modifications with respect to the choice of analytical lines used, the same statement can be made for spectrochemical impurity methods.

8.2 METHODS OF ANALYSIS FOR HAFNIUM

The Separation and Quantitative Determination of Hafnium (and Zirconium)

Classical methods, primarily precipitometric, for the separation and quantitative determination of zirconium and hafnium as a single entity are described in several excellent reference books [2-4]. Portcastle [5] has summarized methods used up to 1953 for the separation and determination of zirconium (and hafnium). The referenced works have placed considerably greater emphasis on the analytical chemistry of zirconium. Provided herein is a review of some of the older chemical techniques which have not diminished in importance and a critical summary of the more recent developments in the analytical chemistry of the two elements.

Precipitation and Gravimetric Methods

Both hafnium and zirconium can be precipitated as the hydrous oxides from neutral or basic solutions, but, in general, this does not serve as an efficient separation from many other metals in the mix-

tures normally encountered. The ignited oxides are, however, the most important weighing forms for the two elements.

One of the most effective methods for the separation of hafnium and zirconium from other metals is by precipitation as the phosphates from strong mineral acid solution [6]. Only tantalum, niobium, thorium, and protactinium interfere to yield high results. The interference due to thorium can be eliminated by dissolution of the phosphate and reprecipitation. Much has been written about the unsatisfactory stoichiometry of the ignited phosphate precipitate $[\text{Zr}(\text{Hf})\text{P}_2\text{O}_7]$ as a weighing form. Depending upon the compositions of wash solutions used, more or less phosphate may be hydrolyzed from the precipitate. Claassen and Visser [7] have reinvestigated the method and have shown that a reproducible, stoichiometric pyrophosphate is obtained under controlled conditions.

When ammonium acid phosphate is used as the precipitant, the precipitate obtained is usually quite voluminous and gelatinous. Willard and Hahn [8] obtained dense, crystalline precipitates by the method of precipitation from homogeneous solution. Phosphate is generated in the acid solution by the hydrolysis of either trimethylphosphate or metaphosphoric acid. The precipitate is ignited as usual to the pyrophosphate for weighing purposes. The method has the disadvantage that a long period of standing (12 to 15 hours) is necessary for complete precipitation.

Various other precipitants such as phenylarsonic acid, n-propylarsonic acid, tannin, cupferron, selenious acid, potassium iodate [2-4], and mandelic acid and its derivatives [9, 10] have been used with varying degrees of success for the separation of hafnium and zirconium from other elements. Of these, the mandelic acids and cupferron are the most useful for a wide variety of separations. Precipitation as the cupferrate with subsequent ignition to the oxide serves to separate hafnium and zirconium from elements such as hexavalent uranium, aluminum, chromium, and the alkaline earths. Iron, titanium, niobium, tantalum, silicon, and tungsten, among others, accompany the hafnium and zirconium.

Mandelic acid, introduced by Kumins [9] and studied by Hahn [10], serves to separate hafnium and zirconium from titanium, iron, vanadium, aluminum, chromium, thorium, cerium, tin, barium, calcium, copper, bismuth, antimony, cadmium, cobalt, magnesium, manganese, mercury, nickel, uranium, and zinc. Zirconium and hafnium are precipitated from hydrochloric acid solution, and the precipitate is filtered and washed with a solution of the reagent and usually ignited to the oxide. The superior selectivity of the reagent has led to further studies of the use of it and other glycolic acid derivatives

for the precipitation of zirconium and hafnium. Whereas Kumins ignited the precipitate to the oxide, Astanina and Ostroumov [11] found that the mandelate precipitate could be washed free of excess reagent with alcohol, dried, and weighed directly as the tetramandelate. These authors found no interference from the rare earths and molybdenum. Jonckers [12] showed that the active group of mandelic acid is the -CHOHCOOH portion and found that nine other acids containing this glycolic acid group demonstrated the same specific precipitating properties as mandelic acid. Hahn and Joseph [13] studied the precipitation of hafnium and zirconium with 1-naphthyl-glycolic acid from hydrochloric acid solution. For zirconium, a digestion period of 20 minutes at 85°C gave complete precipitation, whereas 30 minutes of digestion was necessary to accomplish complete precipitation of hafnium. Separations from iron, aluminum, thorium, titanium, lanthanum, uranium, and tin were accomplished. The authors found no particular advantages for the reagent over mandelic acid. Oesper and Klingenberg [14] and Klingenberg and Papucci [15] investigated the precipitating properties of the *p*-chloro and *p*-bromo derivatives of mandelic acid and found that the latter was the best of the mandelic acids yet considered. Both reagents give a greater volume of precipitate, the precipitate can be washed with distilled water, less time is needed for the formation of the precipitate, and only about one-tenth as much reagent is used in comparison with the unsubstituted acid. These authors suggested the possibility that the precipitate could be weighed directly after being washed with alcohol and being dried at 100°C instead of being ignited to the oxide. Hahn [16] used the method of direct weighing of the bromomandelate precipitate to determine hafnium-zirconium ratios. The validity of the direct-weighing technique was challenged by Belcher, Sykes, and Tatlow [17] who obtained erratic results with mandelic and *p*-bromo-mandelic acids unless the precipitates were ignited to the oxide. The apparent lack of reproducibility of the direct-weighing technique has been shown by Hahn and Baginski [18] to be due to the formation of basic zirconium mandelates. These authors demonstrated that stoichiometric tetramandelates are obtained by precipitating from hot, strongly acid (5M or more) solutions.

Although precipitation from hydrofluoric acid solution as barium fluozirconate or fluohafnate has received little attention, it is a useful method, particularly for separation from niobium. Hume [19] developed the method for the determination of zirconium activity in fission-product mixtures with particular emphasis on the separation from niobium. Telford [20] applied the method to the analysis of uranium-niobium-zirconium alloys for zirconium content. The

zirconium is separated as the fluozirconate and subsequently determined by dissolving and reprecipitating as the cupferrate. This procedure has been further evaluated by Milner and Barnett [21] who completed the determination with a chelatometric titration. Milner and Barnett also reported satisfactory separations from titanium, tantalum, molybdenum, tungsten, lead, iron, copper, and tin.

In view of their superior selectivity and ease of use, the phosphates and mandelic or p-bromomandelic acid are the two leading reagents available for the separation and determination of hafnium and zirconium. The variety of conflicting information found in the literature on both reagents by no means detracts from their value. The varying reports on the nonstoichiometry of the pyrophosphates and mandelates doubtlessly arise from different conditions of acidity of precipitation and methods of washing the precipitates. Because of the ease with which the precipitates are converted to the oxides, mandelic acid and its derivatives appear to be the more suitable reagents for a great many separations. If ignition is carried to the oxide stage, very little attention need be given to conditions such as acidity of precipitation and methods of washing the precipitates.

Volumetric Methods

The lack of a second valence state stable in aqueous solution precludes the application of redox volumetric methods to the quantitative determination of hafnium and zirconium. Various other volumetric methods such as alkalimetric, precipitometric, and fluoride complexometric titrations have been proposed but have met with only limited application. The application of chelatometric methods to the titration of the two elements has received widespread attention in the past few years and fills a long-felt need for rapid volumetric methods.

Fritz and Fulda [22] describe the titration of zirconium and hafnium with ethylene diamine tetra-acetic acid (EDTA) at pH 1.4, using Eriochrome Cyanine RC or Alizuroil Cyanine RC as indicators. In a very extensive interference study, it was found that a number of metals and nonmetals, notably thorium, molybdenum, ferric iron, fluoride, sulfate, and tartrate, interfere. The iron interference can be eliminated by prior reduction to the ferrous state. A procedure of considerably greater selectivity has recently been described by Fritz and Johnson [23]. An excess of standard EDTA is added to the solution of zirconium at pH 2.0, and the excess is back-titrated with a solution of bismuth nitrate, using thiourea as

the indicator. Because few cations form stronger complexes than bismuth and zirconium, very few elements interfere with the method. Of thirty-one metallic elements tested, only arsenious, ferric, mercurous, molybdate, nickel, and stannic tin interfere. Further, zirconium can be determined in the presence of phosphate, sulfate, thiocyanate, tartrate, and small amounts of fluoride.

Bricker and Sweetser [24] add an excess of standard EDTA solution to the acetate-buffered zirconium solution and back-titrate spectrophotometrically with ferric iron. Milner and Phennah [25] carry out a mandelate separation and determine the zirconium by the addition of excess EDTA and back-titration with ferric iron at pH of 5.0 to 6.0 using salicylic acid as a visual indicator. Milner and Edwards [26] improved the precision of this method by the use of spectrophotometric indication of the end point of the back-titration. Either benzohydroxamic or salicylic acid is used as the spectrophotometric indicator.

Olson and Elving [27, 28] have developed a precipitometric amperometric titration of hafnium and zirconium with cupferron which is applicable in the presence of phosphate and large amounts of fluoride. Iron, titanium, and other metals which are precipitated by cupferron interfere. The method has been applied to the determination of zirconium in uranium-zirconium and uranium-niobium-zirconium mixtures. In the latter mixture, zirconium is separated as the phosphate prior to the amperometric titration [29]. In view of the relative instability of cupferron solutions, these methods offer little or no advantage over those using EDTA.

The reagent 1-nitroso-2-naphthol has been used by Wilson and Rhodes [30] to titrate zirconium solutions amperometrically in an acetate-buffered medium. Copper, nickel, cobalt, and iron, among others, interfere with the titration. For most hafnium and zirconium-bearing materials, a prior separation would be mandatory.

Usatenko and Bekleshova [31] have revived the complexometric titration of zirconium with fluoride by using an electrometric end-point indication. The zirconium solution is titrated at pH 2.0 with a standard solution of sodium fluoride. The endpoint is determined amperometrically with a rotating platinum electrode using ferric iron as the indicating ion. It is stated that calcium, magnesium, titanium, chromic, and ferrous ion do not interfere, while aluminum and beryllium cause positive interference.

Colorimetric Methods

Relatively few satisfactory reagents have been proposed for the colorimetric estimation of hafnium and zirconium. Table 8.1 summarizes a number of color reagents which have been studied to 1957.

Notable among elements and ions which interfere with the various methods are iron, titanium, thorium, tin, aluminum, phosphate, and fluoride. Since the occurrence of these elements in admixture with zirconium and hafnium is quite frequent, the analyst is almost invariably faced with the necessity of separating the two elements from them prior to the colorimetric determination. The use of reagents such as p-dimethylaminoazophenylarsonic acid (parasonic acid), the mandelic acids, and phosphates, which may be used to effect separations and subsequent indirect determinations of the two elements, is, therefore, quite attractive when one is confronted with a rather complex mixture. Parasonic acid has been used first to isolate and then to determine as little as one microgram of zirconium. The work of Grimaldi and White [44] who used the reagent to isolate as little as 0.1 microgram prior to colorimetric determination with quercetin indicates that the arsonic acid could be made much more sensitive by a few modifications in the technique of precipitation. Similarly, Hahn and Weber [50] used mandelic acid to precipitate and then to determine zirconium by dissolving the precipitate and measuring the absorbance of the phenyl group of the precipitant. Bricker and Waterbury [49] note that p-bromomandelic acid has been used to determine microgram amounts of zirconium in a similar manner but indicated that the method was highly dependent on the source of the reagent used. Instead of dissolving the precipitate and measuring the absorbance of the p-bromomandelate complex, these authors resorted to the use of chloranilic acid to determine the zirconium content of the precipitate. In view of the fact that they were able to isolate as little as 12 micrograms of zirconium by precipitation, further study of the method of direct absorbance measurement should be fruitful.

Of the other reagents listed in Table 8.1, alizarin [37-40] remains as one of the most useful for the determination of the two elements. Although it is not as sensitive as may be desired for certain applications, alizarin is relatively simple to use and is at least no more subject to interference than any of the other direct-color reagents so far proposed. From the standpoint of high sensitivity, the reagent quercetin, applied by Grimaldi and White [44], is superior to most other reagents but is subject to a myriad of interferences. Parasonic acid precipitation effectively isolates zirconium from the majority of interferences, however, and as little as 0.1 microgram of zirconium or hafnium can be determined with quercetin after the separation.

Two useful fluorescence methods, using 3-hydroxyflavone (flavonol) [52] and morin [53], have been proposed in the last few years. Both reagents are reasonably selective and can be used to determine as

little as 3 to 5 micrograms of the two elements. Both are subject to interference by ferric iron, but the interference is easily circumvented by removal with mercury cathode electrolysis or reduction to the ferrous state. The morin method involves measurement of the fluorescence before and after the addition of EDTA. The zirconium and hafnium-morin fluorescence is destroyed by the chelating agent, but that of aluminum, gallium, thorium, uranium, tin, and antimony is not, thereby effectively eliminating interference by these elements.

There has been relatively little investigation of the fundamental reactions occurring between zirconium and hafnium and the color-forming reagents. Studies by Liefhafsky and his co-workers [37-39] on the formation of hafnium and zirconium lakes with alizarin indicate that the lakes are true 1:1 chemical compounds rather than absorption complexes. These investigators proposed a structural formula for the hafnium lake involving two primary valence bonds to the hafnyl portion of the molecule. Gubeli and Jacob [54] measured the dissociation constants of the alizarin complexes of hafnium and zirconium and found 2.3 and 1.5×10^{-7} , respectively, thus adding further evidence that these lakes are true chemical compounds. Thamer and Voigt [45] identified 1:1 and 1:2 complexes of zirconium and chloranilic acid, the former being the more predominant. Structural formulas for both complexes were proposed, and the similarity to the oxalate complexes was noted.

Although slight differences in stability are generally expected for most hafnium and zirconium complexes, the differences are by no means sufficient to distinguish between the two elements. On a mole-to-mole basis, all of the color reagents studied to date either have been shown to react, or may be expected to react, with both elements in an identical manner. Probably the most fruitful area of research yet to be explored lies not in attempting to develop reagents which will distinguish between the two elements, but rather in developing reagents which are more selective in determining both elements in the presence of other ions, notably iron and the Group IV elements.

Solvent-Extraction Methods

The increased application of solvent-extraction techniques in recent years has provided the analyst with an important new tool for the separation of hafnium and zirconium from other elements. The two most important new classes of extraction reagents for zirconium and hafnium are the fluorinated diketones and the alkyl phosphoric acids. Most of the investigation of these reagents has been aimed at methods for the separation of the two elements from each other; however, a few papers have dealt with the separation

from other elements. In these papers, little emphasis is placed on the separation of hafnium from other elements, but under the conditions used it would also be extracted quantitatively with zirconium.

Conditions for the quantitative extraction of zirconium from nitric acid solution and separations from other elements with 2-thenoyltrifluoroacetone (TTA) have been studied by Moore [55]. Essentially complete extraction is attained from 2 to 12M nitric acid solutions, using 0.5M TTA in xylene; 2M hydrochloric acid serves equally well. The zirconium can be quantitatively stripped back to an aqueous nitric-hydrofluoric acid phase. Separations from the alkali and alkaline earth metals, trivalent rare earths, stannous tin, cobalt, trivalent chromium, uranyl, thorium, ferrous iron, aluminum, bismuth, niobium, protactinium, and ferric iron (6M hydrochloric acid) were achieved. Up to 4.4 mg/ml of zirconium can be extracted from 10M nitric acid.

Scadden and Ballou [56] isolated zirconium and niobium in concentration of 1 mg/ml from nearly all of the other fission products by extraction with 0.6M di-n-butyl phosphoric acid in n-butyl ether from a solution containing 1M sulfuric acid, 2.5M ammonium sulfate, and 0.004M oxalic acid. The two elements can be back-washed from the organic phase with 4M hydrofluoric acid. If the aqueous phase contains, in addition, 6 percent hydrogen peroxide, 95 percent or more of the zirconium (1 mg/ml) is extracted with a 0.06M solution of the reagent, whereas only 1 percent of the niobium is extracted, thus effecting a moderately satisfactory separation of the two elements.

J. C. White [57] has reported initial studies on the use of various trialkylphosphine oxides for the extraction of hafnium and zirconium and other elements. Both elements are completely extracted from 1 to 7M hydrochloric acid solution with a 0.1M solution of tri-n-octylphosphine oxide in cyclohexane and from 7M hydrochloric acid with a 0.1M solution of tris-2-ethyl-n-hexyl phosphine oxide. The latter reagent is somewhat more selective, apparently because of the steric influence of the methyl group. Further studies of extractions with other alkyl-phosphine oxides from various media may well increase the selectivity of this class of reagents.

Various other reagents of limited selectivity have been used for the extraction separation of hafnium and zirconium from other elements. Of these, cupferron and 8-quinolinol [58] are the most useful, but they do not approach the selectivity of the first two reagents described above.

Ion-Exchange Methods

Of the more modern methods available for the separation of hafnium and zirconium from other elements, ion-exchange tech-

niques are among the most valuable. Although most of the initial investigations of these techniques were for the purpose of separating the two elements from one another, quite a number of studies have recently been devoted to the separation of zirconium and hafnium from other elements.

Table 8.2 summarizes the more important fundamental papers which describe methods of separation from other elements. Because hydrofluoric acid is commonly used to effect solution of many hafnium and zirconium materials, media containing this acid are quite practical from the standpoint of laboratory operations. Quantitative separations of milligram and gram amounts of zirconium and hafnium from milligram and gram amounts of aluminum [64], niobium, tantalum, titanium, and iron [65] have been accomplished in hydrofluoric-hydrochloric acid media.

The extensive fundamental studies of Kraus and others [66] on the adsorption characteristics of hafnium and zirconium and numerous other elements from hydrochloric acid and hydrochloric-hydrofluoric acid media suggest many possible separations from other elements. Future application of these and other such studies will greatly simplify some of the difficult problems of the past in the analytical chemistry of hafnium and zirconium.

TABLE 8.2—ION-EXCHANGE SEPARATIONS OF ZIRCONIUM AND HAFNIUM FROM OTHER ELEMENTS

| RESIN | ELUANT | AMOUNT OF ZR AND/OR HF | SEPARATED | REMARKS | REF. |
|-----------------------------|------------------------------------|---------------------------|--|---|------|
| Amberlite IR100 (cation) | Water solution of $ZrO(NO_3)_2$ | About 100 mg. | Fe, Ti, rare earths, Be | Zr passes through column as a colloidal solution. Column on H or Na cycle. | 59 |
| Dowex 1 (anion) | 1M HCl 0.01M $H_2C_2O_4$ | Tracer..... | Cs, Ce, Pr, Nb | Order of elution: Cs, Ce, Pr, Zr, Nb. | 60 |
| Dowex 1 (anion) | 0.2-9M HCl 0.004- 17M HF | Tracer..... | Nb..... | Zr precedes Nb. Best separations in 1.0M HCl-0.5M HF. | 61 |
| Dowex 1 (anion) | HCl-HF and NH_4Cl | 1 mg Zr..... | Pa, Nb, Ta... | Order of elution: Zr, Pa (9M HCl-0.004M HF), Nb (9M HCl-0.18M HF), Ta (4M NH_4Cl - 1M HF). | 62 |
| Dowex 2 (anion) | HCl..... | Tracer..... | Nb (Ta)..... | Study of K_d for Hf, Zr, Nb, Ta. Zr washed through column with 6-7M HCl. Nb eluted with 1.5-4.0N HCl. | 63 |
| Dowex 1 (anion) | 0.06M HCl-0.08M HF | 1 g..... | Al from Zr, Hf | Determination of Al in Zr (and Hf). Al eluted; others left on column. | 64 |
| Anion resins..... | HCl, HCl-HF, etc. | Tracer..... | Summary of separations feasible in HCl and other media. Adsorption data given for 60 elements in HCl solution. | | 66 |

The Quantitative Separation of Hafnium from Zirconium

Most research on the separation of hafnium from zirconium has been directed toward commercial-scale separation, primarily for atomic energy uses. These methods of separation—solvent extraction, ion exchange, fractional crystallization or precipitation, fractional distillation, etc.—are described in Chapter 2 of this book and will not be covered here, except for a brief mention of some of the more promising procedures from an analytical viewpoint. Because many of these processes involve multiple batch or continuous operation, their use for quantitative analytical chemistry applications has been rather limited with the exception of certain of the ion-exchange techniques. Further, a rapid increase in the availability of precise and rapid spectrochemical methods for the determination of the two elements in the presence of each other has tended to de-emphasize the development of analytical chemical methods of separation.

Since ion-exchange techniques lend themselves most readily to laboratory-scale separations, their application is the most promising approach to separations from a quantitative analytical viewpoint. A number of authors have described quantitative or near-quantitative separations based on elution from cationic or anionic exchange resins by the use of various complexing agents. Table 8.3 sum-

TABLE 8.3—ADSORPTION SEPARATIONS OF HAFNIUM FROM ZIRCONIUM

| ADSORPTION MATERIAL | ELUANT OR SOLVENT | Hf AND Zr | DEGREE OF SEPARATION | REF. |
|-----------------------|--|----------------------------|---|------|
| Dowex 50 (cation).... | 6 M HCl..... | 50 mg of oxides.... | Yield 66% of HfO_2 containing about 0.1% ZrO_2 . Total yield 80%. | 67 |
| Dowex 50 (cation).... | 6 M HCl..... | 2 g of oxides..... | Yield 42% of HfO_2 of 99.9% purity. | 68 |
| Dowex 50 (cation).... | 6 M HCl..... | gram quantities... | Yield 25 g of Zr containing <0.01% Hf. | 69 |
| Dowex 50 (cation).... | 1M H_2SO_4 | 900 mg..... | Complete..... | 70 |
| Dowex 50 (cation).... | 0.09M citric 0.45M HNO_3 ... | 270 mg..... | Complete Total yield, 97% | 71 |
| Dowex 1 (anion)..... | 0.5M HF 1.0M HCl..... | Tracer Zr 0.2 mg Hf. | Yield approx. 16% Hf of >95% purity. | 72 |
| IRA 400 (anion)..... | 0.2M HCl 0.1M HF..... | 30 mg..... | Yield 69% of Zr with <0.01% Hf, 69% of Hf with <0.03% Zr. Total yield, 96%. | 73 |
| IRA 400 (anion)..... | 0.22M HCl 0.00008M HF. | 400 mg..... | Hf completely absent in 98% of recovered Zr. | 74 |
| Dowex 2 (anion)..... | 9.0M HCl..... | 7.6 mg..... | Nearly complete..... | 63 |
| Silica gel..... | MCl_4 in methyl alcohol; 1.2M HCl in methyl alcohol for elution for HfCl_4 . | 455 g MCl_4 | 22.5 g of Zr with 0.15% Hf. | 75 |
| Paper..... | 30 ml HNO_3 +70 ml dichlorotriethylene glycol | 150 micrograms.... | Complete..... | 76 |

marizes a number of adsorption-type separations which are promising from an analytical standpoint. Of the various methods listed, those of Lister [70], Benedict, Schumb and Coryell [71], and Huffman, Iddings and Lilly [63] appear to have the greatest potential for application to analytical chemical separations, primarily because these methods yielded virtually complete separation of the two elements. It should be noted, however, that complete separation is unnecessary if a radioisotope of either hafnium or zirconium is added to the mixture prior to separation. One need only isolate a fraction of the element of interest in a pure form and determine its specific activity. From prior knowledge of the initial activity, the amount of the element in the original mixture can then be calculated according to the method of isotopic dilution.

The paper chromatographic technique of Kember and Wells [76] is interesting from the standpoint of complete separation and ease of operation. Further investigation of the separation of various ratios of the two metals, particularly the extremes encountered in reactor-grade hafnium and zirconium, would be worthwhile. For economic reasons, separation by means of liquid-liquid extraction has taken precedence over ion exchange insofar as the large-scale separation of hafnium from zirconium is concerned. Because of the relative complexity of the equipment needed for continuous liquid-liquid extraction, this method is somewhat less attractive for analytical-scale separations. Laboratory-scale counter-current extraction apparatus is, however, commercially available, and analytical separations, using the various complexing or chelating reagents, are entirely feasible. Of the various reagents which have been investigated for commercial-scale separations, the fluorinated diketones [77-80], tributyl phosphate [81], and thiocyanate [82] show the most promise for possible analytical application.

Indirect Chemical Determination of Hafnium-Zirconium Ratios

Several indirect chemical methods have been described for the determination of hafnium-zirconium ratios. All such methods involve the determination of the total of hafnium and zirconium by two independent chemical methods, one of which is invariably the weighing of a mixture of the pure ignited oxides and the other a gravimetric, volumetric, or spectrophotometric measurement. The composition of the mixture is then obtained by the solution of two simultaneous equations for the two unknown quantities. Alternatively, the amount of either constituent can be determined on the basis of an empirical calibration determined from a fixed weight of known oxide mixtures. Because of the practical analytical limitations on the measurement of the two quantities required, the methods are generally limited to the determination of upwards of 5 to 10 per-

cent of hafnium in zirconium and vice versa. Extremely accurate measurements are required to obtain reasonably reproducible values in the lower percentage ranges, and useful determinations below one percent of either constituent are virtually impossible with normal analytical techniques.

Fujiwara [83] applied the phosphate precipitation method to the determination of hafnium content of zirconium salts. The two metals are isolated as the pure ignited oxides, weighed, dissolved, reprecipitated with ammonium phosphate, and ignited to the pyrophosphates for the second weighing. Fujiwara [84] later described the reverse procedure; i.e., isolation and weighing as the pyrophosphates, dissolving, reprecipitating as the hydrous oxides, and igniting to the oxides as the second weighing form. The second procedure would appear to be preferable because of the possibility of obtaining a pure hafnium-zirconium fraction from a variety of other elements in the initial step. Both procedures involve the use of phosphate precipitation, a procedure which, while highly selective, has been the subject of much controversy from the standpoint of the stoichiometry of the final weighing form. (See Precipitation and Gravimetric Method Section of this Chapter.)

Wernimont and DeVries [85] described a method based on the increased effect of hafnium over zirconium on the optical rotation of solutions of tartaric acid. A weighed amount of the oxide mixture is dissolved, tartaric acid and sodium hydroxide are added, and the optical rotation of the solution is measured. The ratio of hafnium to zirconium is calculated by an expression obtained by predetermination of the effects of the two elements individually. Samples covering mole ratios of hafnium to zirconium from 0.15 to 0.45 were analyzed.

Claassen [86] first weighed the mixed oxides, dissolved the mixture, and precipitated hafnium and zirconium from an acid solution as the basic selenites. The precipitate was digested to obtain stoichiometric normal selenites, filtered, and either weighed as $M(\text{SeO}_2)_2$ or dissolved and analyzed iodometrically for selenium. Schumb and Pittman [87] modified the method slightly and utilized it to determine hafnium oxide in various mixtures of hafnium and zirconium oxides obtained during a study of the ferrocyanide separation process. The two metal ions were first precipitated as the selenites, and the precipitate was dried at 125 to 140° C. A known weight of the mixed selenites was then decomposed by heating to the mixed oxides for the second weighing. The authors found the method to be accurate to within 0.25 percent when the amount of hafnium oxide present was about 25 percent.

Hahn [16] reviewed the methods available up to 1951 and proposed the use of p-bromomandelic acid as a weighing form to be

used in conjunction with a mixed oxide weight. The p-bromomandelates are precipitated from an acid solution, filtered, dried, weighed, and then ignited to the oxides which are used as the second weighing form. The authors claim a precision and accuracy of ± 0.5 percent absolute for mixtures containing greater than 10 percent hafnium oxide. In view of the selectivity of p-bromomandelic acid and the large gravimetric factor, the procedure is one of the most attractive yet proposed.

Zopatti [88] determined hafnium-zirconium ratios on a fixed weight of mixed oxides in the range of 10 to 90 percent zirconium oxide by measurement of the alizarin red S color developed in a solution of the oxides. To increase the accuracy of the method, Freund and Holbrook [89] utilized a differential spectrophotometric alizarin red S method. In the range of 10 to 50 percent zirconium oxide, the absorbance is measured against a permanent absorbance standard fabricated from strips of colored cellophane. A calibration curve is prepared from known mixtures of hafnium and zirconium oxides all containing the same total amount of the two oxides. Results accurate to a few tenths of a percent are obtained in the indicated range. Using certain instrument modifications, the method should be applicable to the lower hafnium-zirconium ratios encountered in naturally occurring minerals and ores.

Proposed methods based on the analysis of mixed halides, sulfates, or ammonium fluoro salts have not received general application because of the relative difficulty of obtaining such compounds in a reproducibly pure form. Methods based on density measurement of the mixed oxides or other pure compounds have been used but are not popular because of the inherent difficulties in the measurement of the density of such materials [1, 3, 90].

Spectrochemical Methods for the Determination of Hafnium

As discussed in the previous sections, the positive identification of hafnium by classical chemical procedures is complicated by the homologous chemical properties of hafnium and zirconium. As might be expected, however, the optical and X-ray spectra of these elements are not identical, and identification can be made by various spectroscopic techniques. Because of the comparatively low natural abundance of hafnium, direct detection in naturally occurring substances has been rare. Moreover, the spectral sensitivity of the element is poor and, since the oxide is quite refractory, detection below 0.01 percent is usually difficult [91]. Frequently, the isomorphic chemical properties of hafnium and zirconium are used advantageously to concentrate the hafnium chemically into a zirconium matrix which can then be analyzed spectrochemically. Thus,

to a large extent, the lowest limit of detection is predetermined by the ability to detect hafnium in a zirconium base.

Since quantitative spectrochemical methods are inherently empirical, the preparation of synthetic mixtures of hafnium and zirconium is of some importance. Solution procedures offer the most direct approach to placing the sample and synthetic standard in identical form, but most analysts have preferred to work with the oxide powder, since procedures using this form normally have lower limits of detection and are more convenient to handle. Synthetic oxide standards usually are prepared by igniting, at 850°C , the hydroxide precipitates obtained from sulfuric acid solutions of known concentrations. Although hafnium-zirconium alloys should be ideal for direct metal analyses, practical considerations such as sample form or specifications near the limit of optimum spectral sensitivity have often precluded the analysis of this form. With the exception of excitation with the high-voltage spark or triggered arc, point-to-plane excitation is impractical because of the arc instability resulting from formation of the nonconducting oxide.

The Determination of Hafnium by X-Ray Spectroscopy

Simultaneously with the discovery of hafnium, Coster [92] identified and studied its L and M spectra. Shortly thereafter, de-Broglie and Cabrera [93] determined the K absorption edges, and Cook and Stevenson [94] reported observation and measurement of the K emission series. Subsequently, the wave length and intensity measurements for the characteristic lines have appeared in numerous tables, handbooks, and texts [95, 96].

Although the X-ray spectrum of hafnium has been used extensively for its identification and determination, this approach is less favorable, comparatively speaking, than for many other elements. Hafnium is an element of relatively high atomic number, and an applied voltage of approximately 80 is required to excite the intense K lines. Since contemporary commercial instruments normally are not designed to supply this voltage, the analyst is compelled to use the weaker L lines. The use of the L lines is complicated by the presence of zirconium for, by rare coincidence, the first-order hafnium L series is diffracted at approximately the same angle as the second-order zirconium K series. Thus, to some extent, the spectrochemist is afflicted with a problem similar to that confronting the classical chemist. Furthermore, those working in the field prior to the electronic developments of the 1940-50 era were handicapped by the inconvenience of demountable tubes, unstable power supplies, and photographic photometry. Despite these difficulties,

X-ray spectroscopy has been used effectively whenever the demand warranted.

Before the atomic energy program created such a wide interest in the determination of hafnium, most of the determinations for this element were confined to investigations of an academic nature or mineralogical surveys. On the assumption that the intensity produced by each hafnium atom was equal to that produced by an atom of a reference element, Coster and de Hevesy [97] modified their original procedure for determining hafnium in hafnium concentrates by direct line intensity measurements to include the addition of known quantities of tantalum and, later, lutecium as reference elements. The latter element was chosen to reduce errors in photographic measurement resulting from a variable background. In 1927, Kimura [98] reported the detection of hafnium in the minerals alvite, hegatalite, and oyamalite and described a procedure for the determination of hafnium in the mixed oxides or phosphates. Rankama [99] discussed the separation of niobium, tantalum, zirconium, and similar elements from their mineral base prior to X-ray spectroscopic examination.

Since the middle 1940's, the nuclear energy program has created a renewed interest in the determination of hafnium, particularly in the presence of zirconium. Fortunately, coincidental with this new incentive has been the evolution of vastly improved fluorescent X-ray instruments and techniques. In 1950, Birks and Brooks [100] described three possible procedures for increasing the effectiveness of the hafnium determination at the zirconium-rich end of the zirconium-hafnium system. Method A described a spectrometer with a special 16-inch collimator for resolving the $\text{HfL}_{\beta 2}$ and the adjacent $\text{HfL}_{\beta 1}$ plus second-order $\text{ZrK}_{\beta 1}$. Method B proposed the comparison of an unresolved hafnium and zirconium line pair with a resolved zirconium line, and method C suggested the reduction of the excitation voltage to a value below that required to excite the zirconium K spectrum. Method C was said to have practical limitations, but the limits of detection for A and B, using reasonable counting times, were estimated to be as low as 0.1 percent Hf. The stated accuracy for method A was 5 to 10 percent and for B about 4 percent.

Studies of the X-ray absorption of hafnium and zirconium have also been made, but there has been little practical application of this work. Canchois and MacTaggart [101] have described a differential absorption procedure for the study of zirconium-hafnium solutions, and Zemany and his associates [102] have investigated the absorption of monochromatic and polychromatic X-rays in mixtures of zirconia and hafnia.

Various practical applications of the basic emission technique have been published. Fujiwara [103] has utilized an X-ray fluorescent procedure to study the formation of hafnium and zirconium metal-

loids and draw conclusions concerning their relative affinities for carbon, nitrogen, and oxygen. Mortimore and Romans [104], using a special collimator similar to that described by Birks and Brooks, have employed fluorescent X-ray analysis to control a zirconium-hafnium separations plant. Their procedure consisted of blending the combined oxides with a corn starch binder, compressing the mixture into a briquette, and comparing the fluorescent X-ray intensities of $\text{HfL}_{\beta 2}$ and ZrK_{β} . The intensity ratio was referred to an analytical curve based upon synthetic standards. The coefficient of variation was stated to be 3.8 percent at a concentration level of 10 percent hafnium and 0.75 percent at a concentration of 40 percent hafnium. Recently, Vainshtein, *et al.* [105], have reported the use of an X-ray spectrograph to determine hafnium in a zirconium matrix at the 0.2 to 0.3 percent level. The Russian group reportedly eliminated the zirconium interference by using low excitation voltages (about 18 kv), yet were able to measure the hafnium intensity. Tantalum and lutetium were added as reference elements. Despujols and Lombroso [106] have been able to extend the detection limit to 0.016 percent hafnium using an aluminum monocrystal spectrometer.

The Determination of Hafnium by Optical Spectroscopy

Much of the essential information required for optical spectrochemical analysis was published long before a great need for its practical application existed. Hensen and Werner [107] obtained hafnium concentrated from Coster and de Hevesy and measured approximately 750 arc and spark lines in the optical region. Peterson [108] observed the spectral lines in the region 2,500 to 3,500 Å, and, subsequently, purer salts were supplied to Meggers [109] who reported the existence of some 1,500 hafnium lines between 2,150 and 9,250 Å. Harrison [110] has included approximately the same number of lines in his "Wavelength Tables." Term analyses for both the neutral and the ionized atoms have been published in the extensive works of Meggers and Scribner [111, 112], and Finkelburg [113] has contributed to the measurement of first ionizational potential. Based upon the fundamental contributions of these workers, the spectrochemical determination of hafnium has become a routine operation in many laboratories.

Prior to 1940, the principal application of optical spectroscopy to the detection of hafnium was in the field of mineralogy. The methods employed were qualitative or, at best, semiquantitative, with the primary purpose being the detection or identification of some of the rarer elements from various mineral sources. Pina de Rubies and Aguado [114] studied the intensity of hafnium lines produced by discharging a mixture of sodium chloride and known quantities of hafnium.

By equilibrating certain spectral lines of hafnium and molybdenum, they were able to estimate the hafnium content in some minerals. Kennard and Howell [115] and Morgan and Auer [115] reported the detection of small quantities of hafnium in zircons. Undoubtedly, similar observations were made in a number of laboratories; however, further discussion of this work is not warranted.

With the development of the atomic energy program, the necessity for determining hafnium at low concentration levels became imperative, and the disclosure of numerous procedures began in 1949. Conway and Moore [117] have described a copper-spark technique [118] which, according to Huffman [119], was modified for use with graphite electrodes. The method was capable of detecting 0.1 microgram of hafnium and had a reported precision of 5 to 10 percent. At approximately the same time, Feldman [120] published his study of hafnium-zirconium mixtures using a porous-cup electrode [121] and condensed, high-voltage spark excitation of sulfuric acid solutions. The procedure covered the hafnium concentration range of 0.1 to 10.0 percent, with an indicated accuracy of ± 2.5 percent of the amount present. Shortly thereafter, Fassel and Anderson [122] reported their exhaustive investigation of hafnium-zirconium ratios from 0.001 to 100 percent using a single exposure. An overdamped condenser discharge was used to excite a briquetted mixture of the combined oxides and flake graphite. By taking advantage of the similar chemical and physical characteristics of these elements, and carefully selecting analytical line pairs, they were able to obtain standard deviations of 1.5 to 2.0 percent over wide variations in analytical parameters.

Numerous other procedures can be cited in the literature but will be mentioned only briefly. Kingsburg and Temple [123] have described a procedure for depositing oxides on flat graphite rods and determining hafnium from 0.01 to 55 percent. Various a-c and d-c arc techniques were described in the minutes of the Zirconium Analytical Conference [124] held at Massachusetts Institute of Technology in March 1952, and Mortimore and Noble [125] have outlined a procedure using the d-c arc and a BaF_2 buffer which is particularly applicable to hafnium contents between 0.003 and 0.4 percent.

Kryuger, *et al.* [126], have analyzed for hafnium in the range between 0.01 and 15.0 percent, using an oxide-graphite-sodium pyrophosphate mixture and the d-c arc. The reputed accuracy of this procedure is ± 1.5 percent. Additional references pertaining to various modifications of these basic procedures can all be found in the literature [127-134].

8.3 THE ANALYSIS OF HAFNIUM METAL FOR IMPURITY CONTENT

Sampling

Three forms of hafnium metal are normally encountered in the atomic energy field, viz, sponge, crystal bar, and arc-melted ingot. As with zirconium and titanium, the sampling of sponge metal presents problems arising from the segregation of impurity elements. These effects are minimized, but not eliminated, by the use of rather large (5- to 10-gram) samples for impurity analysis. The method of Gilbert and Morrison [135] for sampling zirconium sponge by briquetting and drilling is somewhat unsatisfactory for hafnium sponge because of the more brittle nature of the latter material.

Carborundum Metals [136] uses this procedure for sampling for magnesium and chlorine analysis only. Samples for other impurity analyses are obtained from a small arc-melted button of the metal prepared from a representative sample of the sponge.

While the impurity content of crystal-bar hafnium is considerably lower than that of sponge, occasionally problems in segregation are still encountered [137]. For acceptance purposes, these problems are largely circumvented by the use of well-mixed, representative, chip samples.

Arc-melted hafnium ingots are usually sampled by drilling or lathe-turning at top and bottom positions to provide representative chip samples for quality control or acceptance purposes. Depending on the quality of the ingot, occasional problems may be encountered in the segregation of tungsten and copper which are at times accidentally and nonuniformly added to the ingot by the arc-melting process. Similar problems are frequently encountered in the sampling and analysis of shapes fabricated from arc-melted ingots.

Because of the great affinity of hafnium and zirconium for the atmospheric gases, analyses for oxygen and nitrogen are best carried out on solid samples rather than chip samples in order to avoid gas absorption caused by the machining techniques required to obtain the latter type of sample. Some success in obtaining machine chip samples for gas analysis has been obtained by taking, at a low rate of feed, as heavy a chip or turning as possible. The tool tip may be cooled by directing a stream of air at the point of contact with the material.

Chemical Methods of Analysis for Impurities in Hafnium

As with other analytical techniques previously discussed, the analysis of hafnium for impurities employs methods identical to those used for zirconium. A number of monographs have been published on the subject of the analysis of zirconium for impurities [138-141].

The methods described in these publications can be used without modification for the determination of the impurity content of hafnium metal.

Methods of dissolution of hafnium and zirconium are also identical. Both metals are readily soluble in hydrofluoric or fluoboric acids. The metals also dissolve slowly in hot, concentrated sulfuric acid. About 5 percent of water accelerates the dissolution in sulfuric acid by making the resulting sulfate salts soluble. Both metals are also slowly dissolved by heating in aqua regia.

Because of the similarity of methods for zirconium and hafnium impurity analysis, only those methods which are used for the analysis of major impurity elements in reactor-grade hafnium will be discussed. For detailed outlines of the methods for these and other elements, the reader is referred to the monographs on the analysis of zirconium.

Nitrogen

This element is normally determined by solution of the sample in hydrofluoric and hydrochloric acids, steam distillation of the resulting ammonia from a strongly basic solution, and colorimetric or titrimetric determination of ammonia in the distillate [139-142]. For the low nitrogen contents normally encountered in crystal-bar or arc-melted ingot samples, the colorimetric determination of ammonia with Nessler reagent is preferred. Vacuum fusion methods have not been widely applied to the determination of nitrogen because of the difficulty of recovering all the nitrogen in the sample and the complexity of the method in comparison with the solution technique.

Titanium

The yellow color produced by the reaction of titanium with hydrogen peroxide in sulfuric or perchloric acids is used to determine this element. The color can also be developed in hydrofluoric-sulfuric acid solution in which the fluoride ion has been complexed with boric acid [139, 140]. In either case, correction must be made for the interfering colors of vanadium and molybdenum peroxy compounds.

Iron

The most widely used method is the colorimetric procedure, based on the formation of the ferrous -1,10 phenanthroline complex as described by Ayers and Banks [143]. The color is developed in a neutral tartrate buffered solution by the addition of a reducing agent such as hydroxylamine hydrochloride and -1,10 phenanthroline. Precipitation of hafnium or zirconium in the neutral solutions is

prevented by complex formation with tartrate or citrate ion. The solutions must be heated at about 60° C for one-half hour to attain full color development [140, 143]. Center [139] has described the application of the thiocyanate method to the determination of iron in zirconium metal.

Copper

This element is usually determined by chloroform extraction of the yellow-colored, cuprous-neocuproine complex from a neutral tartrate-buffered solution. Fluoride ion present from hydrofluoric acid dissolution is complexed with boric acid [139, 140]. The use of neocuproine for the determination of copper in a wide range of materials has been extensively investigated by Smith and McCurdy [144] and Gahler [145]. The reagent is almost ideal from the standpoint of lack of interferences. No elements present in hafnium or zirconium interfere with the method.

Aluminum

Freund and Miner [64] have described an anion-exchange procedure for the determination of aluminum in zirconium. Zirconium is adsorbed on the resin from a hydrochloric-hydrofluoric acid solution, and aluminum is determined in the eluate with aluminum after separation of the residual zirconium and iron by extraction of the cupferrates of these metal ions into chloroform. Chromium, if present, is separated by volatilization as chromyl chloride. Goward and co-workers [140] modified the procedure by separating interfering impurities in the eluate by mercury cathode electrolysis, extracting aluminum as the 8-quinolinolate into chloroform, and measuring the fluorescence intensity of the resulting extract. Although hafnium is less strongly adsorbed by the anion resin than zirconium, the adsorption is sufficient to effect the separation of hafnium from aluminum. Consequently, the method for the determination of aluminum in hafnium is identical with that for zirconium. Eberle [139] has described a fluorimetric method for the determination of aluminum with Pontachrome Blue Black R after separation of the zirconium by precipitation with salicylic acid. The method has not been widely accepted by the zirconium-hafnium industry.

Tungsten

A number of variations of the thiocyanate method have been applied to the determination of tungsten in hafnium and zirconium. The method of Freund [146] is the most widely accepted procedure [139, 140]. Samples are dissolved in hydrofluoric and nitric acids, and the solutions are fumed with sulfuric acid. Tungsten is reduced

in a strongly acidic chloride solution with stannous chloride, and a yellow-colored tungsten (V) complex is formed by the addition of potassium thiocyanate. Greenberg [147] has described the application of the dithiol method to the determination of tungsten in titanium, tantalum, and zirconium. The method appears to have no advantages over the thiocyanate method for zirconium and hafnium metal.

Oxygen

The hydrogen chloride volatilization method of Read and Zoppatti [139, 148], developed for the determination of oxygen in zirconium, has been applied to hafnium metal. Zirconium or hafnium is volatilized at elevated temperature with dry hydrogen chloride. Oxygen remains unvolatilized as the metal oxide and is determined either by weighing the residue or by analyzing it for zirconium or hafnium content. Stanley, *et al.* [149], and Sloman and Harvey [150] have described the application of iron-bath vacuum-fusion techniques to the determination of oxygen in zirconium. Other investigators have reported only limited success with the iron-bath technique [151]. Smiley [152], using an inert-gas-fusion technique, has reported the successful determination of oxygen in a number of refractory metals using a platinum bath. A limited amount of investigation of the method for the analysis of hafnium and zirconium has been done by personnel of Laboratory Equipment Corporation [153]. The results are quite promising, but further investigation is still necessary. The application of the platinum-bath technique by Westinghouse and National Research Corporation to the vacuum-fusion method has yielded results in good agreement with the hydrogen chloride volatilization method for the determination of oxygen in zirconium. It is presumed that the method is equally applicable to the determination of oxygen in hafnium. The bromine-carbon method developed by Codell and Norwitz [154, 155], principally for titanium, has been applied by the authors to the analysis of zirconium for oxygen content. The sample is reacted with bromine and carbon in a heated tube to yield oxygen as carbon monoxide which is subsequently converted to the dioxide, adsorbed on ascarite, and weighed. Results in agreement with the hydrogen chloride method of Read have been obtained for low-oxygen (less than 500 ppm) hafnium [156]. Some difficulty is encountered in the analysis of zirconium if the oxygen content exceeds 1,000 ppm in that complete reaction of the oxide may be difficult to obtain. This difficulty may be circumvented by the use of a graphite boat and intermittent mixing of the oxide-carbon mixture [156]. In any case, the method will not compete with some of the faster methods being developed at this time. Fassel and Gordon [157] have recently described a spectographic method for the determination of oxygen in metals.

Oxygen is evolved as carbon monoxide in an argon atmosphere by d-c arcing the sample in the presence of platinum in a graphite electrode. The resulting carbon monoxide is determined in the argon by d-c arc excitation and measurement of the 7,771 Å oxygen line. The method yields results for the determination of oxygen in zirconium in satisfactory agreement with those obtained by the hydrogen chloride volatilization and platinum-bath fusion methods.

Zirconium

Indirect methods for the determination of hafnium-zirconium ratios are described in a preceding section. Since the zirconium content of commercial hafnium generally lies below 2 percent, the various indirect methods are not applicable to the analysis of this material. Although it is conceivable that one of the previously described ion-exchange techniques for the separation of hafnium from zirconium could be applied to this determination, such a method would be only of academic interest in comparison with the rapid spectroscopic methods available for the routine determination of this impurity.

Emission Spectrometric Determination of Impurities in Hafnium

The effort expended to develop and validate spectrochemical procedures for the determination of impurities in hafnium has been governed to a large extent by the requirements of the atomic energy program, and, with only a few exceptions, there has been little necessity for exacting analyses. As a result, semiquantitative estimates have been used extensively for routine process control. Since zirconium reduces the thermal neutron cross section of hafnium and is normally present in concentrations above 1 percent, a rigorous method frequently is desirable for its determination. Likewise, the accurate determination of copper and tungsten is of some importance, since these elements are likely to be introduced during melting and fabrication and may affect the behavior of the metal significantly.

The Determination of Zirconium in Hafnium

Since the early work of Coster and de Hevesy [1], the logical approach to the determination of major quantities of zirconium in a hafnium matrix has been X-ray spectroscopy, and, with the instruments currently available to the analyst, this determination can be conveniently made with a high degree of accuracy. As mentioned previously, Mortimore and Romans [104] have described the application of this technique to the control of a hafnium-zirconium separations plant; modifications of this procedure have been used by others, including Fassel [158] and the authors. All of the aforementioned analysts have converted the incoming samples to a com-

mon combined oxide form prior to analysis in order to simplify standardization and accommodate a wide variety of sample forms. The synthetic oxide standards are usually prepared by ignition of the combined hydroxides which have been precipitated from solutions of known concentration. Mortimore and Romans have reported the use of corn starch as a binder for briquetting the combined oxides, whereas the authors have used alpha-cellulose for this purpose. Standard briquettes prepared with the latter binder have been used for years, apparently with no ill effects. Since gross errors are likely to be introduced if the sample and standard oxides do not have comparable properties, both should be prepared by identical procedures and reduced to a minus 200-mesh size prior to briquetting. To obtain correct results for oxides which have been prepared by the ignition of metal turnings, appropriate adjustments must be made to the analytical curve derived from synthesized standards. It is believed that the recent introduction of simplified solution attachments for X-ray fluorescent equipment will encourage the development of solution procedures in which sample and synthetic standard will always have the same form.

Gray and Fassel [159] have been able to extend the determination of zirconium in hafnium to the 0.001 percent level with the optical spectrograph. Determinations within the range 0.001 to 0.2 percent zirconium are obtained by d-c arc excitation of an oxide graphite mixture, whereas determinations between 0.1 and 0.5 percent are made by excitation of a conducting briquette with an arc-like, over-damped condenser discharge. The coefficients of variation for the two procedures are approximately 8 percent and 4 percent, respectively.

The Spectrochemical Determination of Impurities in Hafnium

Because most hafnium specifications list the maximum impurity concentration for such elements as aluminum, calcium, copper, chromium, iron, magnesium, manganese, molybdenum, nickel, lead, silicon, tin, titanium, vanadium, and tungsten in the parts per million range, optical spectroscopy has been used extensively for their routine detection. Most of the laboratories performing these analyses have been closely associated with large zirconium operations; hence, it has been common practice to take advantage of the similar properties exhibited by the two elements and to apply the same procedures to the analysis of both. For convenience, and in some instances because of the scarcity of high-purity hafnium, some spectrochemists have analyzed hafnium with analytical curves based upon synthetic zirconium oxide standards. Such procedures correlate relative intensities to concentrations and require the appropriate gravimetric correction. Should the preparation of a high-purity matrix

material be a necessity, fractional crystallization of the oxychloride or ion-exchange procedures appear to be the most practical approach to the removal of impurities from a relatively impure raw material.

A number of analysts have described procedures for the determination of impurities in zirconium which presumably can be adapted to the analysis of hafnium. Chandler [119] and Norris [129] have described procedures which incorporate the addition of cobalt as an internal standard. The former mixes the oxide with graphite and excites a small portion of the mixture in a d-c arc which is stabilized with a rotating magnet. The latter excites the graphite-oxide mixture containing a small quantity of cobalt in a d-c arc to determine some of the refractory and more prevalent impurities but resorts to a AgCl-AgBr-BaF_2 carrier-buffer mixture for the lesser impurities.

Fassel and his co-workers [160] have described a procedure for the determination of the impurities aluminum, calcium, chromium, copper, iron, nickel, magnesium, silicon, and titanium in zirconium. The procedure should also be applicable to the analysis of hafnium. The method employs the excitation of an oxide-graphite conducting briquette with an overdamped condenser discharge. The reported coefficients of variation are approximately 5 percent, indicating that such a procedure is extremely useful for the intermediate concentration levels when specification limits are approached.

Because of the refractory nature of hafnium oxide and, to some extent, the complexity of the hafnium spectrum, many analysts have preferred to work with either buffered or carrier [161] type excitation. It is evident, however, that no single additive will be the best for the determination of every impurity. Kall [162] has added BaF_2 to his sample and reported considerable success by arcing the mixture and using zirconium oxide standards. Similar success using a mixture of AgCl and Ga_2O_3 has been reported by Romans [163] who has also employed an adaptation of the Fassel conducting-briquette technique for the determination of aluminum, iron, chromium, magnesium, titanium, nickel, and manganese. The latter procedure employs standards synthesized from a high-purity HfO_2 matrix. A silver chloride carrier procedure similar to that described by Spitzer and Smith [164] has been used with some success at Westinghouse, and satisfactory agreement between chemical and spectrochemical determinations has been obtained for aluminum, titanium, copper, and iron. Other additives which have been proposed are SrCl_2 , SrF_2 , and CuF_2 .

Presumably, the procedure delineated by Hettel and Fassel [165] for the determination of certain rare earths in zirconium is applicable to the determination of rare earths in hafnium. This procedure effectively combines ion exchange and spectrochemical practices

into a single method which enables the analyst to determine extremely small concentrations of gadolinium, terbium, dysprosium, holmium, and samarium. First, the anion complex of the matrix metal is placed on an anion resin, then the rare earths are eluted and collected on an yttrium carrier which also serves as the internal standard for the spectrochemical procedure. Experimental data indicate good recoveries and acceptable precision.

Other procedures which have appeared in the literature as procedures for the analysis of zirconium are enumerated and summarized in Table 8.4.

Recently, considerable progress has been made in the development of point-to-plane procedures [170, 171] for the determination of impurities in zirconium, and it can safely be presumed that, should the quantity of work warrant the costly preparation and evaluation of metallic standards, these procedures can be extended to include the determination of impurities in hafnium. The excitation sources most commonly being employed for these developments are high-energy, unidirectional, arc-like discharges or triggered a-c arcs. In general, greatly improved precision can be expected from such developments, and, in addition, the direct excitation of the metal form provides a rapid means of confirming homogeneity. Determinations obtained with the current techniques, however, are likely to be influenced by metallurgical history and/or alloying constituents, and because of the small volume of production material to be tested, it is unlikely that point-to-plane procedures will be economically feasible in the near future.

TABLE 8.4—PROCEDURES FOR THE DETERMINATION OF IMPURITIES IN ZIRCONIUM WHICH HAVE APPLICABILITY TO THE ANALYSIS OF HAFNIUM

| SAMPLE FORM | EXCITATION | ADDITIONS | EST. COEFF. VAR. | REFERENCE |
|----------------|------------|--------------------------------|------------------|-----------|
| Oxide | a-c arc | Graphite or AgCl | ± 20 % | 165 |
| Oxide | d-c arc | Graphite briquette | ± 15 % | 134 |
| Oxide or metal | a-c arc | None | ± 30 % | 166 |
| Solution | d-c arc | Lucite-cup | ± 5 % | 167 |
| Oxide | h-v spark | Ga ₂ O ₃ | | |
| | | SrCl ₂ | | |
| | | None | | 168 |
| | | In | | |
| Oxide | d-c arc | Ga ₂ O ₃ | | |
| | | Graphite | | 169 |

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Chapter 9

THERMODYNAMIC PROPERTIES OF HAFNIUM AND ITS COMPOUNDS

By K. K. KELLEY¹ and E. G. KING¹

9.1 INTRODUCTION

Experimental thermodynamic data for hafnium and its compounds are few in number and scattered as to substances. There is no substance for which data are complete, although they are nearly so for the dioxide. By estimating lacking data, it is possible to discuss the metal, the dioxide, the nitride, the carbide, and the four tetrahalides. Data for these substances are assembled in tabular form and are followed by thermodynamic values for the reduction-chlorination of the dioxide and the over-all reductions of the tetrachloride by magnesium and sodium.

Future experimental work undoubtedly will show many of the estimated data to be inadequate. However, without these estimates even a brief chapter, such as this, could not have been prepared. It is hoped that the present availability of pure hafnium in quantity will induce completion of experimental data for the metal and accelerate the synthesis of adequate compounds for use in thermal measurements so that the estimated values may be replaced by experimental results in the near future.

9.2 BASIC DATA

Metal

Hafnium metal has a hexagonal close-packed structure at ordinary temperatures. Conflicting reports of the temperature of the transformation from the hexagonal to the body-centered cubic form are discussed in Chapter 7 which indicates that 2,033° K is the most probable value. It was also indicated in Chapter 7 that the melting point of 2,495° K, determined by Deardorff and Hayes [1], is the best estimate available.

¹ U.S. Bureau of Mines.

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Future experimental work undoubtedly will show many of the estimated data to be inadequate. However, without these estimates even a brief chapter, such as this, could not have been prepared. It is hoped that the present availability of pure hafnium in quantity will induce completion of experimental data for the metal and accelerate the synthesis of adequate compounds for use in thermal measurements so that the estimated values may be replaced by experimental results in the near future.

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The low temperature heat capacity of hafnium metal was measured by Cristescu and Simon [2] (13–210° K) and by Weertman, Burk and Goldman [3] (unpublished measurements, 50–200° K). The former workers observed a large heat capacity maximum at 75° K. This was not substantiated by the latter investigators, nor by Burk and Darrell [4]. As a consequence, the entropy is taken as $S^{\circ}_{298.15} = 10.91$ cal/deg mole, in accordance with the calculations of Stull and Sinke [5] from the data of Weertman, Burk, and Goldman.

Neither the heat content nor heat capacity of hafnium above 298° K has been measured, making it necessary to estimate values if thermodynamic calculations involving hafnium are to be conducted. Estimations for crystalline and liquid hafnium to 3,000° K were made by Stull and Sinke [5]. Their values of heat content above 298.15° K and entropy are adopted and listed in Table 9.1, after rounding to the nearest 10 cal and after adjustment to conform with the melting temperature of 2,495° K found by Deardorff and Hayes [1]. Because of the large uncertainty regarding the transition temperature existing at the time, Stull and Sinke minimized the estimations by assuming only a single crystalline phase below the melting point. Therefore, the values in Table 9.1 at temperatures above 2,033° K are subject to correction for the heat of transformation, the magnitude of which is undetermined.

Stull and Sinke [5] computed thermodynamic properties of monatomic hafnium gas to 3,000° K from spectroscopic data. Their values of the heat content (rounded to the nearest 10 cal) and entropy again are adopted and appear in Table 9.2.

The only vapor pressure information is a roughly measured boiling point reported by Richardson [6] (5,400° K) and an estimate of the boiling point by Brewer [7] (5,500° K). Stull and Sinke [5] have combined their estimated thermal data with Brewer's estimate of the boiling point to obtain heats and free energies of sublimation and vaporization to 3,000° K. In this Chapter their results have been modified (a) to take account of the change in melting temperature and (b) by altering somewhat the extrapolation of the heat content and entropy which is necessary for bridging the gap between 3,000 and 5,500° K. The adjusted values of the heat and free energy of sublimation and vaporization appear in Table 9.3, and the course of the vapor pressure-temperature relationship is shown in Table 9.4.

Dioxide

Hafnium dioxide is the only hafnium-containing substance for which basic thermodynamic data are substantially complete. The ordinary monoclinic variety of this substance is stable to around 1,873° K, according to Curtis, Doney, and Johnson [8]. These

workers report the melting point as $3,178^{\circ}\text{K}$, while Brewer [9] gives $3,063^{\circ}$. Skinner, Beckett, and Johnston [10], select $3,048^{\circ}\text{K}$ as the melting point and $5,673^{\circ}\text{K}$ as the boiling point.

The heat of formation of the dioxide from the elements at 298.15°K was measured by Humphrey [11] as -266.06 ± 0.28 kcal/mole. The low temperature heat capacity (52 – 298°K) was measured by Todd [12] and the entropy was evaluated as $S^{\circ}_{298.15} = 14.18 \pm 0.10$ cal/deg mole. Orr [13] measured the high temperature heat content to $1,804^{\circ}\text{K}$.

Table 9.5 contains the heat content increments (above 298.15°K) and entropy values of hafnium dioxide. Orr's data were extrapolated to $2,000^{\circ}\text{K}$.

Table 9.6 contains heat and free energy of formation values to $2,000^{\circ}\text{K}$. These results differ from those published by Coughlin [14] because of the use of different entropy and high temperature heat content values for hafnium metal. (The heat content and entropy values for oxygen are given in Tables 9.39 to 9.55 along with data for other nonhafnium substances.)

Nitride

The only experimental thermal value available for hafnium nitride is the heat of formation which was determined by Humphrey [11]. High temperature heat content and entropy values have been estimated by the present authors in Table 9.7, for use in obtaining the heats and free energies of formation in Table 9.8. Brewer and co-workers [15] give $3,580^{\circ}\text{K}$ as the melting point and state that the nitride has an equilibrium pressure of 10^{-5} atm. at $2,500^{\circ}\text{K}$.

Carbide

No experimental heat data exist for hafnium carbide. The present authors estimate the heat of formation as $\Delta H^{\circ}_{298.15} = -44.7$ kcal/mole. This is based upon Mah and Boyle's [16] value for zirconium carbide in comparison with the known heats of formation of dioxides [11, 17] and nitride [11, 18] of hafnium and zirconium. The high temperature heat content and entropy values also are estimated. The results appear in Tables 9.9 and 9.10. Brewer and co-workers [15] list $4,160^{\circ}\text{K}$ as the melting point of hafnium carbide and state that the substance is slowly volatile in high vacuum at $2,500^{\circ}\text{K}$. Skinner, Beckett, and Johnston [10] and Agte and Moers [19] also select $4,160^{\circ}\text{K}$ as the melting point.

Tetrafluoride

The only thermal data in the literature for hafnium tetrafluoride are estimates. Brewer and co-workers [20] list -436 kcal/mole as

the heat of formation at 298.15° K. Brewer [21] also estimates the melting and normal boiling points to be coincident at $1,200^{\circ}$ K, and the heats of fusion and sublimation to be 18 and 45 kcal/mole. These values are used in conjunction with our estimates of the entropies and heat contents (Tables 9.11 and 9.12) to obtain the heats and free energies of formation and sublimation (Tables 9.13, 9.15, and 9.16) and the vapor pressure in Table 9.14.

Tetrachloride

The low temperature heat capacity of hafnium tetrachloride (52 – 298° K) was measured by Todd [12] and the entropy obtained as $S^{\circ}_{298.15} = 45.6 \pm 0.6$ cal/deg mole. Orr [13] measured the high temperature heat content to 486° K. Brewer and co-workers [20] estimate the heat of formation as -255 kcal/mole. Brewer [21] gives the melting point as 705° K and estimates the heat of fusion as 10.5 kcal/mole. He also lists 590° K as the 1-atm sublimation point and 24 kcal/mole as the heat of sublimation, in accordance with the work of Fischer, Gewehr, and Wingchen [22]. The present authors estimate the high temperature heat content of the gas as shown in Table 9.18. These data are combined to obtain the heats and free energies of formation, the heats and free energies of sublimation, and the sublimation pressure, given in Tables 9.17 to 9.22.

Tetrabromide

Brewer [21] gives 693° K as the melting point of hafnium tetrabromide and 595° K as the normal sublimation point. He estimates the heat of fusion as 10 kcal/mole and gives 24 kcal/mole as the heat of sublimation, adopting the measurements of Fischer, Gewehr, and Wingchen [22]. Brewer and co-workers [20] estimate the heat of formation at 298.15° K from the metal and gaseous diatomic bromine to be -225 kcal/mole. All other values employed in compiling Tables 9.23–9.28 were estimated by the present authors.

Tetraiodide

The heat of formation of hafnium tetraiodide was estimated by Brewer and co-workers [20] as -175 kcal/mole at 298° K, from gaseous diatomic iodine and metal. Brewer [21] estimates the melting point as 750° K, the heat of fusion as 11 kcal/mole, the normal sublimation point as 700° K, and the heat of sublimation as 28 kcal/mole. All other data necessary for compiling Tables 9.29–9.34 were estimated by the authors.

Hydride

In their study of the equilibrium phase relationships between hafnium and hydrogen Veleckis and Edwards [40] calculated in detail

thermodynamic properties for the various solid phases of 779° C. Details pertinent to pressure-concentration isotherms are to be found in Chapter 6. The calculations covered the concentration range of 0 to 57 atom percent H_2 in hafnium and thus included the α phase, 0 to 8.67 a/o; the $\alpha + \delta$ region, 8.67 to 34.5 a/o; and the δ phase ranging from 34.5 to 57 a/o.

Figure 9.1 is a plot of the logarithm of equilibrium H_2 pressure vs reciprocal absolute temperature for varying concentrations of hydrogen in hafnium. The slopes of these curves yield the relative partial molal enthalpies. The curve t-t of Figure 9.1 is taken for the ($\alpha - \delta$) two-phase region, and its slope yields the "apparent" relative partial molal enthalpy of hydrogen in $\alpha + \delta$. The relative partial molal enthalpies of the α and δ phases along with the "apparent" quantities for ($\alpha - \delta$) were then used to calculate the integral enthalpy of mixing ($\Delta H'$) of hydrogen with hafnium by means of the Gibbs-Duhem equation. The relative partial molal enthalpies are illustrated graphically in Figure 9.2.

The relative partial molal free energies for hydrogen ($\Delta \bar{F}_{H_2}$) were obtained from the equilibrium pressure data, and, by use of the Gibbs-Duhem equation, the relative partial molal free energy value for Hf ($\Delta \bar{F}_{Hf}$) and integral values for the formation of solid solution ($\Delta F'$) were determined. These data are shown in Figure 9.3. The entropy

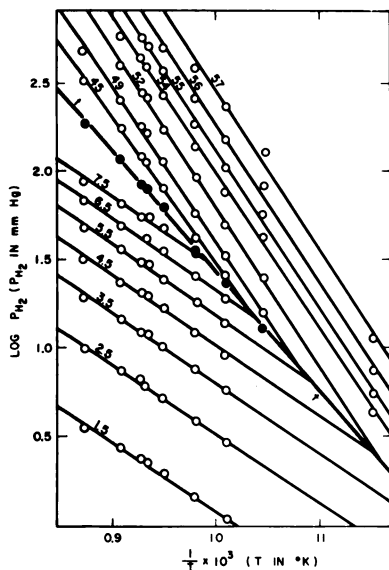


FIGURE 9.1. Pressure-Temperature Curves for the Composition Range 1.5 to 57 Hydrogen Atomic Percent.

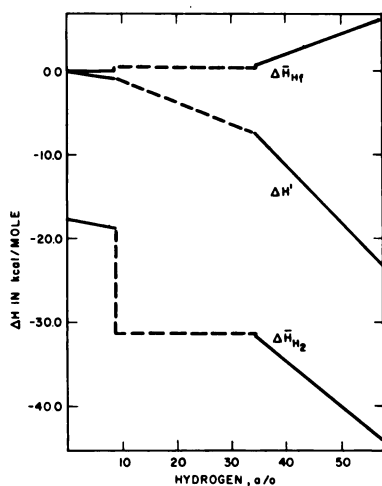


FIGURE 9.2. Relative Partial Molal and Integral Enthalpies for H_2 -Hf System at 779° C ($\Delta H'$ in kcal/gram Atom Hf).

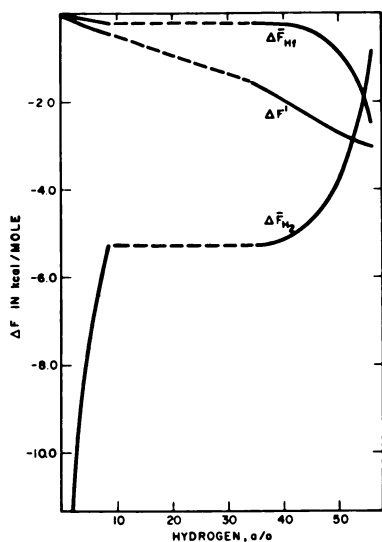


FIGURE 9.3. Relative Partial Molal and Integral Free Energies for H-Hf System at 779° C ($\Delta F'$ in kcal/gram Atom Hf).

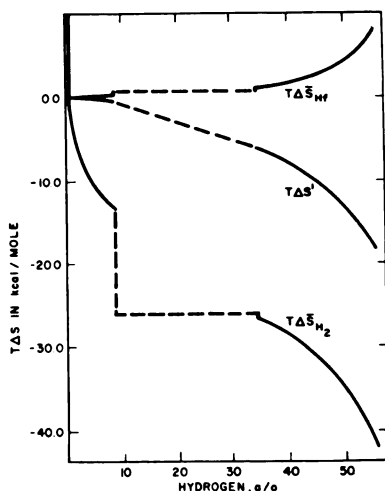


FIGURE 9.4. Relative Partial Molal and Integral Entropies for H-Hf System at 779° C ($T\Delta S'$ in kcal/gram Atom Hf.)

data of Figure 9.4 were then obtained from the free energies and enthalpies. It is emphasized that all values are for a temperature of 779° C only.

Other Substances

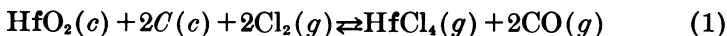
The melting point of hafnium boride (HfB) is 3,608° K, according to Agte and Moers [19]. This is 70° higher than the melting point of the corresponding zirconium boride.

Gruen and Katz [23] have reported 628° K as the normal boiling point of the hafnium chloride-phosphorus oxychloride complex ($3\text{HfCl}_4 \cdot 2\text{POCl}_3$) and 20.5 kcal/mole as its heat of vaporization. The same authors give 633° K and 20.5 kcal/mole for the corresponding zirconium compound.

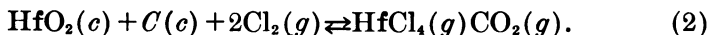
9.3 METALLURGICAL REACTIONS

Reduction-Chlorination of Hafnium Dioxide

One of the steps of extractive metallurgy of hafnium is the reduction-chlorination of the dioxide to produce hafnium tetrachloride, according to the reactions



and



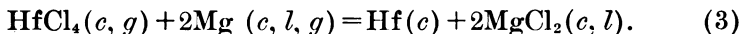
The heats and free energies of these reactions are assembled in Tables 9.35 and 9.36, along with data for the corresponding reactions involving the analogous zirconium compounds.

Reaction (1) is exothermic throughout the temperature range 298–2,000° K, while the corresponding zirconium reaction is slightly endothermic at temperatures below 1,400° K, according to the data in Table 9.35. Although the heat values for the hafnium reaction involve an estimated heat of formation of hafnium tetrachloride, it is highly probable that the indicated difference in reaction heats (approximately 20 kcal) is real. Brewer and co-workers' [20] estimated heat of formation of zirconium tetrachloride has been substantiated by experiment and there is no reason to believe that their similarly made estimate for hafnium tetrachloride should be seriously in error.

Reaction (2) is highly exothermic as is the corresponding zirconium reaction. From the free energy standpoint, reaction (2) predominates at temperatures below about 1,000° K; reaction (1) predominates above 1,000° K. Both reactions are thermodynamically potent and theoretically will go to virtual completion. Comparison of reduction-chlorination free energy data for the dioxides of hafnium, zirconium, and titanium shows that at 1,000° K the potency of reaction increases in the order zirconium-titanium-hafnium.

Magnesium Reduction of Hafnium Tetrachloride

The Kroll process for producing hafnium metal involves the reduction of hafnium tetrachloride by magnesium:



This reaction undoubtedly occurs in three steps which, in turn, produce trichloride, dichloride, and metal. At present, no thermodynamic data exist for the lower chlorides of hafnium and, as a consequence, only the over-all reaction is calculable. Table 9.37 gives heat and free energy values for reaction (3) and for the corresponding reaction to produce zirconium.

TABLE 9.3—VAPORIZATION DATA FOR HAFNIUM (c, l)

| T(°K) | ΔH_v° (kcal/mole) | ΔF_v° (kcal/mole) | P(atm) |
|--------------------|-----------------------------------|-----------------------------------|-----------------------|
| 298.15 | 167.8 | 157.8 | ----- |
| 400 | 167.7 | 154.4 | ----- |
| 500 | 167.6 | 151.0 | ----- |
| 600 | 167.4 | 147.7 | ----- |
| 700 | 167.3 | 144.4 | ----- |
| 800 | 167.2 | 141.2 | ----- |
| 900 | 167.2 | 137.9 | ----- |
| 1,000 | 167.1 | 134.7 | ----- |
| 1,100 | 167.0 | 131.4 | ----- |
| 1,200 | 166.9 | 128.2 | ----- |
| 1,300 | 166.9 | 125.0 | ----- |
| 1,400 | 166.8 | 121.8 | ----- |
| 1,500 | 166.8 | 118.6 | ----- |
| 1,600 | 166.7 | 115.3 | ----- |
| 1,700 | 166.7 | 112.1 | ----- |
| 1,800 | 166.6 | 108.9 | ----- |
| 1,900 | 166.5 | 105.7 | ----- |
| 2,000 | 166.4 | 102.5 | ----- |
| 2,100 | 166.3 | 99.3 | 4.6×10^{-11} |
| 2,200 | 166.2 | 96.2 | 2.8×10^{-10} |
| 2,300 | 166.1 | 93.0 | 1.5×10^{-9} |
| 2,400 | 166.0 | 89.8 | 6.7×10^{-9} |
| 2,495 ¹ | 165.8 | 86.8 | 2.5×10^{-8} |
| 2,495 | 160.0 | 86.8 | 2.5×10^{-8} |
| 2,500 | 160.0 | 86.6 | 2.7×10^{-8} |
| 2,600 | 160.0 | 83.7 | 9.2×10^{-8} |
| 2,700 | 159.9 | 80.7 | 2.9×10^{-7} |
| 2,800 | 159.8 | 77.8 | 8.5×10^{-7} |
| 2,900 | 159.7 | 74.9 | 2.3×10^{-6} |
| 3,000 | 159.6 | 72.0 | 5.7×10^{-6} |

¹ Melting point.

TABLE 9.4—VAPOR PRESSURE OF HAFNIUM (c, l)

| T(°K) | P(atm) | T(°K) | P(atm) |
|-------|------------|-------|-----------|
| 2,140 | 10^{-10} | 3,360 | 10^{-4} |
| 2,280 | 10^{-9} | 3,720 | 10^{-3} |
| 2,430 | 10^{-8} | 4,170 | 10^{-2} |
| 2,610 | 10^{-7} | 4,740 | 10^{-1} |
| 2,820 | 10^{-6} | 5,500 | 1 |
| 3,070 | 10^{-5} | | |

TABLE 9.5—HEAT CONTENT AND ENTROPY OF $\text{HfO}_2(\text{c})$

| T(°K) | $H_T^\circ - H_{298.15}^\circ$ (cal/mole) | S_T° (cal/deg mole) | T(°K) | $H_T^\circ - H_{298.15}^\circ$ (cal/mole) | S_T° (cal/deg mole) |
|-------------|--|-------------------------------|-------------|--|-------------------------------|
| 298.15----- | 0 | 14. 18 | 1, 200----- | 16, 230 | 38. 42 |
| 400----- | 1, 540 | 18. 61 | 1, 300----- | 18, 200 | 40. 00 |
| 500----- | 3, 170 | 22. 24 | 1, 400----- | 20, 200 | 41. 48 |
| 600----- | 4, 900 | 25. 40 | 1, 500----- | 22, 220 | 42. 87 |
| 700----- | 6, 710 | 28. 19 | 1, 600----- | 24, 260 | 44. 19 |
| 800----- | 8, 570 | 30. 67 | 1, 700----- | 26, 320 | 45. 44 |
| 900----- | 10, 450 | 32. 88 | 1, 800----- | 28, 400 | 46. 63 |
| 1, 000----- | 12, 350 | 34. 88 | 1, 900----- | 30, 500 | 47. 76 |
| 1, 100----- | 14, 280 | 36. 72 | 2, 000----- | 32, 620 | 48. 85 |

TABLE 9.6—HEAT AND FREE ENERGY OF FORMATION OF $\text{HfO}_2(\text{c})$

| T(°K) | $\Delta H^\circ(\text{f})$ (kcal/mole) | $\Delta F^\circ(\text{f})$ (kcal/mole) | T(°K) | $\Delta H^\circ(\text{f})$ (kcal/mole) | $\Delta F^\circ(\text{f})$ (kcal/mole) |
|-------------|---|---|-------------|---|---|
| 298.15----- | -266. 1 | -252. 4 | 1, 200----- | -262. 9 | -213. 4 |
| 400----- | -265. 9 | -247. 8 | 1, 300----- | -262. 5 | -209. 2 |
| 500----- | -265. 6 | -243. 3 | 1, 400----- | -262. 2 | -205. 2 |
| 600----- | -265. 3 | -238. 9 | 1, 500----- | -261. 8 | -201. 1 |
| 700----- | -264. 9 | -234. 5 | 1, 600----- | -261. 3 | -197. 1 |
| 800----- | -264. 5 | -230. 2 | 1, 700----- | -260. 9 | -193. 1 |
| 900----- | -264. 1 | -225. 9 | 1, 800----- | -260. 5 | -189. 1 |
| 1, 000----- | -263. 7 | -221. 7 | 1, 900----- | -260. 1 | -185. 1 |
| 1, 100----- | -263. 3 | -217. 5 | 2, 000----- | -259. 7 | -181. 2 |

TABLE 9.7—HEAT CONTENT AND ENTROPY OF $\text{HfN}(\text{c})$

| T(°K) | $H_T^\circ - H_{298.15}^\circ$ (cal/mole) | S_T° (cal/deg mole) | T(°K) | $H_T^\circ - H_{298.15}^\circ$ (cal/mole) | S_T° (cal/deg mole) |
|-------------|--|-------------------------------|-------------|--|-------------------------------|
| 298.15----- | 0 | 10. 91 | 1, 200----- | 10, 380 | 26. 62 |
| 400----- | 1, 080 | 14. 02 | 1, 300----- | 11, 640 | 27. 62 |
| 500----- | 2, 170 | 16. 45 | 1, 400----- | 12, 920 | 28. 57 |
| 600----- | 3, 270 | 18. 46 | 1, 500----- | 14, 220 | 29. 47 |
| 700----- | 4, 400 | 20. 20 | 1, 600----- | 15, 550 | 30. 33 |
| 800----- | 5, 550 | 21. 74 | 1, 700----- | 16, 900 | 31. 15 |
| 900----- | 6, 720 | 23. 11 | 1, 800----- | 18, 270 | 31. 93 |
| 1, 000----- | 7, 920 | 24. 37 | 1, 900----- | 19, 670 | 32. 69 |
| 1, 100----- | 9, 140 | 25. 54 | 2, 000----- | 21, 090 | 33. 42 |

TABLE 9.8—HEAT AND FREE ENERGY OF FORMATION OF HfN(c)

| T(°K) | $\Delta H^\circ(f)$ (kcal/mole) | $\Delta F^\circ(f)$ (kcal/mole) | T(°K) | $\Delta H^\circ(f)$ (kcal/mole) | $\Delta F^\circ(f)$ (kcal/mole) |
|-------------|------------------------------------|------------------------------------|------------|------------------------------------|------------------------------------|
| 298.15..... | -88.2 | -81.4 | 1,200..... | -87.2 | -61.6 |
| 400..... | -88.1 | -79.1 | 1,300..... | -87.1 | -59.5 |
| 500..... | -88.0 | -76.9 | 1,400..... | -87.0 | -57.3 |
| 600..... | -87.9 | -74.6 | 1,500..... | -86.8 | -55.2 |
| 700..... | -87.8 | -72.4 | 1,600..... | -86.7 | -53.1 |
| 800..... | -87.7 | -70.2 | 1,700..... | -86.5 | -51.1 |
| 900..... | -87.6 | -68.0 | 1,800..... | -86.3 | -49.0 |
| 1,000..... | -87.5 | -65.9 | 1,900..... | -86.2 | -46.9 |
| 1,100..... | -87.3 | -63.7 | 2,000..... | -86.0 | -44.8 |

TABLE 9.9—HEAT CONTENT AND ENTROPY OF HfC(c)

| T(°K) | $H_T^\circ - H_{298.15}^\circ$ (cal/mole) | S_T° (cal/deg mole) | T(°K) | $H_T^\circ - H_{298.15}^\circ$ (cal/mole) | S_T° (cal/deg mole) |
|-------------|--|-------------------------------|------------|--|-------------------------------|
| 298.15..... | 0 | 10.91 | 1,200..... | 9,590 | 25.26 |
| 400..... | 950 | 13.65 | 1,300..... | 10,810 | 26.23 |
| 500..... | 1,920 | 15.81 | 1,400..... | 12,060 | 27.16 |
| 600..... | 2,920 | 17.63 | 1,500..... | 13,350 | 28.05 |
| 700..... | 3,950 | 19.22 | 1,600..... | 14,670 | 28.90 |
| 800..... | 5,010 | 20.63 | 1,700..... | 16,020 | 29.72 |
| 900..... | 6,110 | 21.93 | 1,800..... | 17,400 | 30.51 |
| 1,000..... | 7,240 | 23.12 | 1,900..... | 18,810 | 31.27 |
| 1,100..... | 8,400 | 24.22 | 2,000..... | 20,260 | 32.01 |

TABLE 9.10—HEAT AND FREE ENERGY OF FORMATION OF HfC(c)

| T(°K) | $\Delta H^\circ(f)$ (kcal/mole) | $\Delta F^\circ(f)$ (kcal/mole) | T(°K) | $\Delta H^\circ(f)$ (kcal/mole) | $\Delta F^\circ(f)$ (kcal/mole) |
|-------------|------------------------------------|------------------------------------|------------|------------------------------------|------------------------------------|
| 298.15..... | -44.7 | -44.3 | 1,200..... | -45.0 | -43.1 |
| 400..... | -44.6 | -44.2 | 1,300..... | -45.0 | -43.0 |
| 500..... | -44.6 | -44.1 | 1,400..... | -45.1 | -42.8 |
| 600..... | -44.6 | -44.0 | 1,500..... | -45.1 | -42.6 |
| 700..... | -44.7 | -43.8 | 1,600..... | -45.1 | -42.5 |
| 800..... | -44.7 | -43.7 | 1,700..... | -45.1 | -42.3 |
| 900..... | -44.8 | -43.6 | 1,800..... | -45.1 | -42.1 |
| 1,000..... | -44.9 | -43.4 | 1,900..... | -45.1 | -42.0 |
| 1,100..... | -44.9 | -43.3 | 2,000..... | -45.1 | -41.8 |

TABLE 9.11—HEAT CONTENT AND ENTROPY OF $\text{HfF}_4(\text{c})$

| T(°K) | $H_T^\circ - H_{298.15}^\circ$ (cal/mole) | S_T° (cal/deg mole) | T(°K) | $H_T^\circ - H_{298.15}^\circ$ (cal/mole) | S_T° (cal/deg mole) |
|-------------|--|-------------------------------|------------|--|-------------------------------|
| 298.15..... | 0 | 31.50 | 1,000..... | 20,500 | 65.96 |
| 400..... | 2,650 | 39.14 | 1,100..... | 23,840 | 69.14 |
| 500..... | 5,360 | 45.18 | 1,200..... | 27,290 | 72.14 |
| 600..... | 8,180 | 50.32 | 1,300..... | 30,840 | 74.99 |
| 700..... | 11,100 | 54.82 | 1,400..... | 34,500 | 77.70 |
| 800..... | 14,130 | 58.86 | 1,500..... | 38,260 | 80.29 |
| 900..... | 17,260 | 62.55 | | | |

TABLE 9.12—HEAT CONTENT AND ENTROPY OF $\text{HfF}_4(\text{g})$

| T(°K) | $H_T^\circ - H_{298.15}^\circ$ (cal/mole) | S_T° (cal/deg mole) | T(°K) | $H_T^\circ - H_{298.15}^\circ$ (cal/mole) | S_T° (cal/deg mole) |
|-------------|--|-------------------------------|------------|--|-------------------------------|
| 298.15..... | 0 | 77.72 | 1,000..... | 16,100 | 105.09 |
| 400..... | 2,200 | 84.06 | 1,100..... | 18,580 | 107.45 |
| 500..... | 4,400 | 88.97 | 1,200..... | 21,100 | 109.64 |
| 600..... | 6,640 | 93.05 | 1,300..... | 23,650 | 111.68 |
| 700..... | 8,930 | 96.58 | 1,400..... | 26,220 | 113.59 |
| 800..... | 11,270 | 99.70 | 1,500..... | 28,800 | 115.37 |
| 900..... | 13,660 | 102.52 | | | |

TABLE 9.13—SUBLIMATION DATA FOR $\text{HfF}_4(\text{c})$

| T(°K) | ΔH_v° (kcal/mole) | ΔF_v° (kcal/mole) | P(atm) |
|--------------------------|-----------------------------------|-----------------------------------|----------------------|
| 298.15..... | 51.2 | 37.4 | ----- |
| 400..... | 50.7 | 32.8 | ----- |
| 500..... | 50.2 | 28.3 | ----- |
| 600..... | 49.6 | 24.0 | 1.8×10^{-6} |
| 700..... | 49.0 | 19.8 | 6.6×10^{-7} |
| 800..... | 48.3 | 15.7 | 5.1×10^{-8} |
| 900..... | 47.6 | 11.6 | 1.5×10^{-8} |
| 1,000..... | 46.8 | 7.7 | 2.1×10^{-8} |
| 1,100..... | 45.9 | 3.8 | 1.8×10^{-1} |
| 1,200 ¹ | 45.0 | 0.0 | 1.0 |

¹ Normal sublimation point.

TABLE 9.14—SUBLIMATION PRESSURE OF $\text{HfF}_4(\text{c})$

| T(°K) | P(atm) | T(°K) | P(atm) |
|----------|-----------|-------------|-----------|
| 625..... | 10^{-8} | 886..... | 10^{-3} |
| 664..... | 10^{-7} | 968..... | 10^{-2} |
| 708..... | 10^{-6} | 1, 072..... | 10^{-1} |
| 758..... | 10^{-5} | 1, 200..... | 1 |
| 817..... | 10^{-4} | | |

TABLE 9.15—HEAT AND FREE ENERGY OF FORMATION OF $\text{HfF}_4(\text{c})$

| T(° K) | $\Delta\text{H}^\circ(\text{f})$ (kcal/mole) | $\Delta\text{F}^\circ(\text{f})$ (kcal/mole) | T(° K) | $\Delta\text{H}^\circ(\text{f})$ (kcal/mole) | $\Delta\text{F}^\circ(\text{f})$ (kcal/mole) |
|-------------|---|---|---------------------------|---|---|
| 298.15..... | -435. 0 | -412. 2 | 800..... | 432. 4 | -375. 1 |
| 400..... | -434. 6 | -404. 5 | 900..... | -431. 7 | -368. 0 |
| 500..... | -434. 1 | -397. 0 | 1, 000..... | -430. 9 | -361. 0 |
| 600..... | -433. 6 | -389. 6 | 1, 100..... | -430. 0 | -354. 1 |
| 700..... | -433. 0 | -382. 3 | 1, 200 ¹ | -429. 1 | -347. 2 |

¹ Normal sublimation point.TABLE 9.16—HEAT AND FREE ENERGY OF FORMATION OF $\text{HfF}_4(\text{g})$

| T(° K) | $\Delta\text{H}^\circ(\text{f})$ (kcal/mole) | $\Delta\text{F}^\circ(\text{f})$ (kcal/mole) | T(° K) | $\Delta\text{H}^\circ(\text{f})$ (kcal/mole) | $\Delta\text{F}^\circ(\text{f})$ (kcal/mole) |
|-------------|---|---|---------------------------|---|---|
| 298.15..... | -383. 8 | -374. 8 | 1, 000..... | -384. 1 | -353. 3 |
| 400..... | -383. 8 | -371. 7 | 1, 100..... | -384. 1 | -350. 3 |
| 500..... | -383. 9 | -368. 7 | 1, 200 ¹ | -384. 1 | -347. 2 |
| 600..... | -383. 9 | -365. 6 | 1, 300..... | -384. 0 | -344. 1 |
| 700..... | -384. 0 | -362. 5 | 1, 400..... | -384. 0 | -341. 1 |
| 800..... | -384. 0 | -359. 5 | 1, 500..... | -384. 0 | -338. 0 |
| 900..... | -384. 1 | -356. 1 | | | |

¹ Normal sublimation point of $\text{HfF}_4(\text{c})$.TABLE 9.17—HEAT CONTENT AND ENTROPY OF $\text{HfCl}_4(\text{c})$

| T(° K) | $\text{H}_T^\circ - \text{H}_{298.15}^\circ$ (cal/mole) | S_T° (cal/deg mole) | T(° K) | $\text{H}_T^\circ - \text{H}_{298.15}^\circ$ (cal/mole) | S_T° (cal/deg mole) |
|-------------|--|--------------------------------------|----------|--|--------------------------------------|
| 298.15..... | 0 | 45. 60 | 500..... | 6, 020 | 60. 99 |
| 350..... | 1, 520 | 50. 30 | 550..... | 7, 540 | 63. 89 |
| 400..... | 3, 010 | 54. 28 | 600..... | 9, 070 | 66. 55 |
| 450..... | 4, 510 | 57. 81 | 700..... | 12, 160 | 71. 31 |

TABLE 9.18—HEAT CONTENT AND ENTROPY OF $\text{HfCl}_4(\text{g})$

| $T(^{\circ}\text{K})$ | $H_T^{\circ}-H_{298.15}^{\circ}$ (cal/mole) | S_T° (cal/deg mole) | $T(^{\circ}\text{K})$ | $H_T^{\circ}-H_{298.15}^{\circ}$ (cal/mole) | S_T° (cal/deg mole) |
|-----------------------|--|---------------------------------|-----------------------|--|---------------------------------|
| 298.15----- | 0 | 89.81 | 1,000----- | 17,700 | 120.15 |
| 400----- | 2,490 | 96.99 | 1,100----- | 20,270 | 122.60 |
| 500----- | 4,980 | 102.54 | 1,200----- | 22,840 | 124.83 |
| 600----- | 7,500 | 107.13 | 1,300----- | 25,420 | 126.90 |
| 700----- | 10,030 | 111.03 | 1,400----- | 28,000 | 128.81 |
| 800----- | 12,580 | 114.44 | 1,500----- | 30,590 | 130.60 |
| 900----- | 15,140 | 117.45 | | | |

TABLE 9.19—SUBLIMATION DATA FOR $\text{HfCl}_4(\text{c})$

| $T(^{\circ}\text{K})$ | ΔH_v° (kcal/mole) | ΔF_v° (kcal/mole) | P(atm) |
|------------------------|-------------------------------------|-------------------------------------|-----------------------|
| 298.15----- | 25.5 | 12.3 | 9.6×10^{-10} |
| 400----- | 25.0 | 7.9 | 4.8×10^{-8} |
| 500----- | 24.5 | 3.7 | 2.4×10^{-7} |
| 590 ¹ ----- | 24.0 | 0.0 | 1.0 |
| 600----- | 23.9 | -0.4 | 1.4 |
| 700----- | 23.4 | -4.4 | 24 |

¹ Normal sublimation point.TABLE 9.20—SUBLIMATION PRESSURE OF $\text{HfCl}_4(\text{c})$

| P(atm) | $T(^{\circ}\text{K})$ | P(atm) | $T(^{\circ}\text{K})$ |
|-----------------|-----------------------|-----------------|-----------------------|
| 10^{-8} ----- | 316 | 10^{-3} ----- | 442 |
| 10^{-7} ----- | 336 | 10^{-2} ----- | 482 |
| 10^{-6} ----- | 357 | 10^{-1} ----- | 530 |
| 10^{-5} ----- | 382 | 1----- | 590 |
| 10^{-4} ----- | 410 | | |

TABLE 9.21—HEAT AND FREE ENERGY OF FORMATION OF $\text{HfCl}_4(\text{c})$

| $T(^{\circ}\text{K})$ | $\Delta H^{\circ}(\text{f})$ (kcal/mole) | $\Delta F^{\circ}(\text{f})$ (kcal/mole) | $T(^{\circ}\text{K})$ | $\Delta H^{\circ}(\text{f})$ (kcal/mole) | $\Delta F^{\circ}(\text{f})$ (kcal/mole) |
|-----------------------|---|---|------------------------|---|---|
| 298.15----- | -255.0 | -233.5 | 590 ¹ ----- | -253.0 | -213.3 |
| 400----- | -254.3 | -226.3 | 600----- | -253.0 | -212.6 |
| 500----- | -253.6 | -219.4 | 700----- | -252.3 | -206.0 |

¹ Normal sublimation point.

TABLE 9.22—HEAT AND FREE ENERGY OF FORMATION OF $\text{HfCl}_4(\text{g})$

| T(° K) | $\Delta H^\circ(\text{f})$ (kcal/mole) | $\Delta F^\circ(\text{f})$ (kcal/mole) | T(° K) | $\Delta H^\circ(\text{f})$ (kcal/mole) | $\Delta F^\circ(\text{f})$ (kcal/mole) |
|------------------------|---|---|------------|---|---|
| 298.15----- | -229.5 | -221.2 | 900----- | -228.7 | -205.1 |
| 400----- | -229.3 | -218.4 | 1,000----- | -228.6 | -202.5 |
| 500----- | -229.2 | -215.7 | 1,100----- | -228.5 | -199.9 |
| 590 ¹ ----- | -229.0 | -213.3 | 1,200----- | -228.5 | -197.3 |
| 600----- | -229.0 | -213.0 | 1,300----- | -228.4 | -194.7 |
| 700----- | -228.9 | -210.4 | 1,400----- | -228.4 | -192.2 |
| 800----- | -228.8 | -207.8 | 1,500----- | -228.4 | -189.6 |

¹ Normal sublimation point of $\text{HfCl}_4(\text{c})$.TABLE 9.23—HEAT CONTENT AND ENTROPY OF $\text{HfBr}_4(\text{c})$

| T(° K) | $H_T^\circ - H_{298.15}^\circ$ (cal/mole) | S_T° (cal/deg mole) | T(° K) | $H_T^\circ - H_{298.15}^\circ$ (cal/mole) | S_T° (cal/deg mole) |
|-------------|--|-------------------------------|----------|--|-------------------------------|
| 298.15----- | 0 | 57.00 | 600----- | 9,900 | 79.74 |
| 400----- | 3,180 | 66.16 | 700----- | 13,480 | 85.26 |
| 500----- | 6,460 | 73.48 | | | |

TABLE 9.24—HEAT CONTENT AND ENTROPY OF $\text{HfBr}_4(\text{g})$

| T(° K) | $H_T^\circ - H_{298.15}^\circ$ (cal/mole) | S_T° (cal/deg mole) | T(° K) | $H_T^\circ - H_{298.15}^\circ$ (cal/mole) | S_T° (cal/deg mole) |
|-------------|--|-------------------------------|------------|--|-------------------------------|
| 298.15----- | 0 | 102.18 | 1,000----- | 18,000 | 133.16 |
| 400----- | 2,590 | 109.67 | 1,100----- | 20,590 | 135.63 |
| 500----- | 5,140 | 115.35 | 1,200----- | 23,180 | 137.89 |
| 600----- | 7,700 | 120.02 | 1,300----- | 25,770 | 139.95 |
| 700----- | 10,270 | 123.98 | 1,400----- | 28,370 | 141.87 |
| 800----- | 12,840 | 127.42 | 1,500----- | 30,970 | 143.67 |
| 900----- | 15,420 | 130.44 | | | |

TABLE 9.25—SUBLIMATION DATA FOR $\text{HfBr}_4(\text{c})$

| T(° K) | ΔH_v° (kcal/mole) | ΔF_v° (kcal/mole) | P(atm) |
|------------------------|-----------------------------------|-----------------------------------|-----------------------|
| 298.15----- | 26. 2 | 12. 7 | 4.9×10^{-10} |
| 400----- | 25. 6 | 8. 2 | 3.3×10^{-8} |
| 500----- | 24. 8 | 3. 9 | 2.0×10^{-3} |
| 595 ¹ ----- | 24. 0 | 0. 0 | 0.0 |
| 600----- | 23. 9 | -0. 2 | 1.2 |
| 700----- | 22. 9 | -4. 2 | 20 |

¹ Normal sublimation point.TABLE 9.26—SUBLIMATION PRESSURE OF $\text{HfBr}_4(\text{c})$

| T(°K) | P(atm) | T(°K) | P(atm) |
|----------|-----------|----------|-----------|
| 320----- | 10^{-8} | 448----- | 10^{-3} |
| 339----- | 10^{-7} | 487----- | 10^{-2} |
| 361----- | 10^{-6} | 534----- | 10^{-1} |
| 385----- | 10^{-5} | 595----- | 1 |
| 414----- | 10^{-4} | | |

TABLE 9.27—HEAT AND FREE ENERGY OF FORMATION OF $\text{HfBr}_4(\text{c})$

| T(° K) | $\Delta H^\circ(\text{f})$ (kcal/mole) | $\Delta F^\circ(\text{f})$ (kcal/mole) | T(° K) | $\Delta H^\circ(\text{f})$ (kcal/mole) | $\Delta F^\circ(\text{f})$ (kcal/mole) |
|-------------|---|---|------------------------|---|---|
| 298.15----- | -225. 0 | -203. 8 | 595 ¹ ----- | -222. 4 | -133. 6 |
| 400----- | -224. 2 | -196. 6 | 600----- | -222. 3 | -183. 3 |
| 500----- | -223. 3 | -189. 9 | 700----- | -221. 2 | -176. 8 |

¹ Normal sublimation point.

TABLE 9.28—HEAT AND FREE ENERGY OF FORMATION OF $\text{HfBr}_4(\text{g})$

| T(° K) | $\Delta H^\circ(\text{f})$ (kcal/mole) | $\Delta F^\circ(\text{f})$ (kcal/mole) | T(° K) | $\Delta H^\circ(\text{f})$ (kcal/mole) | $\Delta F^\circ(\text{f})$ (kcal/mole) |
|------------------------|---|---|------------|---|---|
| 298.15..... | -198.9 | -191.1 | 900..... | -198.0 | -176.1 |
| 400..... | -198.7 | -188.5 | 1,000..... | -197.9 | -173.7 |
| 500..... | -198.5 | -186.0 | 1,100..... | -197.8 | -171.2 |
| 595 ¹ | -198.4 | -183.6 | 1,200..... | -197.8 | -168.8 |
| 600..... | -198.4 | -183.5 | 1,300..... | -197.7 | -166.4 |
| 700..... | -198.2 | -181.0 | 1,400..... | -197.6 | -164.0 |
| 800..... | -198.1 | -178.6 | 1,500..... | -197.6 | -161.6 |

¹ Normal sublimation point of $\text{HfBr}_4(\text{c})$.TABLE 9.29—HEAT CONTENT AND ENTROPY OF $\text{HfI}_4(\text{c})$

| T(° K) | $H^\circ_T - H^\circ_{298.15}$ (cal/mole) | S°_T (cal/deg mole) | T(° K) | $H^\circ_T - H^\circ_{298.15}$ (cal/mole) | S°_T (cal/deg mole) |
|-------------|--|-------------------------------|----------|--|-------------------------------|
| 298.15..... | 0 | 64.50 | 600..... | 10,750 | 89.31 |
| 400..... | 3,550 | 74.74 | 700..... | 14,460 | 95.03 |
| 500..... | 7,110 | 82.68 | 800..... | 18,250 | 100.09 |

TABLE 9.30—HEAT CONTENT AND ENTROPY OF $\text{HfI}_4(\text{g})$

| T(° K) | $H^\circ_T - H^\circ_{298.15}$ (cal/mole) | S°_T (cal/deg mole) | T(° K) | $H^\circ_T - H^\circ_{298.15}$ (cal/mole) | S°_T (cal/deg mole) |
|-------------|--|-------------------------------|------------|--|-------------------------------|
| 298.15..... | 0 | 112.84 | 1,000..... | 18,250 | 144.30 |
| 400..... | 2,650 | 120.48 | 1,100..... | 20,850 | 146.78 |
| 500..... | 5,250 | 126.28 | 1,200..... | 23,450 | 149.04 |
| 600..... | 7,850 | 131.02 | 1,300..... | 26,050 | 151.13 |
| 700..... | 10,450 | 135.03 | 1,400..... | 28,650 | 153.05 |
| 800..... | 13,050 | 138.50 | 1,500..... | 31,250 | 154.85 |
| 900..... | 15,650 | 141.56 | | | |

TABLE 9.31—SUBLIMATION DATA FOR $\text{HfI}_4(\text{c})$

| T(° K) | ΔH_v° (kcal/mole) | ΔF_v° (kcal/mole) | P(atm) |
|------------------------|-----------------------------------|-----------------------------------|-----------------------|
| 298.15----- | 32. 0 | 17. 6 | 1.3×10^{-13} |
| 400----- | 31. 1 | 12. 8 | 1.0×10^{-7} |
| 500----- | 30. 1 | 8. 4 | 2.1×10^{-4} |
| 600----- | 29. 1 | 4. 1 | 3.2×10^{-3} |
| 700 ¹ ----- | 28. 0 | 0. 0 | 1. 0 |
| 800----- | 26. 8 | -3. 9 | 12. |

¹ Normal sublimation point.TABLE 9.32—SUBLIMATION PRESSURE OF $\text{HfI}_4(\text{c})$

| T(° K) | P(atm) | T(° K) | P(atm) |
|----------|-----------|----------|-----------|
| 379----- | 10^{-8} | 525----- | 10^{-3} |
| 400----- | 10^{-7} | 572----- | 10^{-2} |
| 425----- | 10^{-6} | 628----- | 10^{-1} |
| 454----- | 10^{-5} | 700----- | 1 |
| 487----- | 10^{-4} | | |

TABLE 9.33—HEAT AND FREE ENERGY OF FORMATION OF $\text{HfI}_4(\text{c})$

| T(° K) | $\Delta H^\circ(f)$ (kcal/mole) | $\Delta F^\circ(f)$ (kcal/mole) | T(° K) | $\Delta H^\circ(f)$ (kcal/mole) | $\Delta F^\circ(f)$ (kcal/mole) |
|-------------|------------------------------------|------------------------------------|------------------------|------------------------------------|------------------------------------|
| 298.15----- | -175. 0 | -153. 9 | 600----- | -171. 5 | -133. 8 |
| 400----- | -173. 9 | -146. 8 | 700 ¹ ----- | -170. 3 | -127. 6 |
| 500----- | -172. 7 | -140. 2 | 800----- | -169. 0 | -121. 6 |

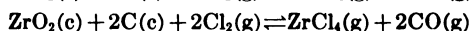
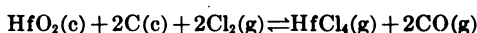
¹ Normal sublimation point.

TABLE 9.34—HEAT AND FREE ENERGY OF FORMATION OF $\text{HfI}_4(\text{g})$

| T(° K) | $\Delta H^\circ(f)$ (kcal/mole) | $\Delta F^\circ(f)$ (kcal/mole) | T(° K) | $\Delta H^\circ(f)$ (kcal/mole) | $\Delta F^\circ(f)$ (kcal/mole) |
|------------------------|------------------------------------|------------------------------------|------------|------------------------------------|------------------------------------|
| 298.15..... | -143.0 | -136.3 | 1,000..... | -141.9 | -121.3 |
| 400..... | -142.8 | -134.0 | 1,100..... | -141.8 | -119.3 |
| 500..... | -142.6 | -131.8 | 1,200..... | -141.8 | -117.2 |
| 600..... | -142.4 | -129.7 | 1,300..... | -141.7 | -115.2 |
| 700 ¹ | -142.3 | -127.6 | 1,400..... | -141.7 | -113.2 |
| 800..... | -142.1 | -125.5 | 1,500..... | -141.6 | -111.2 |
| 900..... | -142.0 | -123.4 | | | |

¹ Normal sublimation point of $\text{HfI}_4(\text{c})$.

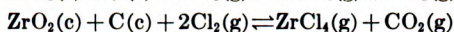
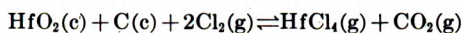
TABLE 9.35—HEATS AND FREE ENERGIES OF THE REACTIONS



| T(° K) | Hf | | Zr | |
|--------------------------|----------------------------|----------------------------|----------------------------|----------------------------|
| | ΔH° (kcal) | ΔF° (kcal) | ΔH° (kcal) | ΔF° (kcal) |
| 298.15..... | -16.3 | -34.4 | 3.8 | -15.2 |
| 400..... | -16.1 | -40.7 | 4.0 | -21.7 |
| 500..... | -16.2 | -46.8 | 3.9 | -28.1 |
| 600..... | -16.4 | -52.9 | 3.7 | -34.5 |
| 700..... | -16.8 | -58.9 | 3.4 | -40.8 |
| 800..... | -17.3 | -64.9 | 3.1 | -47.1 |
| 900..... | -17.9 | -70.9 | 2.6 | -53.3 |
| 1,000..... | -18.4 | -76.8 | 2.1 | -59.5 |
| 1,100..... | -19.0 | -82.6 | 1.6 | -65.7 |
| 1,200..... | -19.7 | -88.3 | 1.0 | -71.7 |
| 1,300..... | -20.3 | -94.0 | 0.5 | -77.8 |
| 1,400..... | -21.0 | -99.6 | -0.1 | -83.9 |
| 1,478 ¹ | ----- | ----- | -0.5 | -88.5 |
| 1,478..... | ----- | ----- | -1.9 | -88.5 |
| 1,500..... | -21.7 | -105.2 | -2.1 | -89.8 |

¹ Transition point of ZrO_2 .

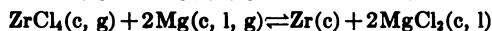
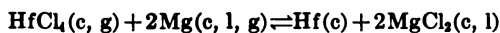
TABLE 9.36—HEATS AND FREE ENERGIES OF THE REACTIONS



| T(° K) | Hf | | Zr | |
|--------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|
| | ΔH° (kcal) | ΔF° (kcal) | ΔH° (kcal) | ΔF° (kcal) |
| 298.15----- | -57.5 | -63.1 | -37.4 | -43.8 |
| 400----- | -57.5 | -65.0 | -37.4 | -46.0 |
| 500----- | -57.7 | -66.8 | -37.5 | -48.1 |
| 600----- | -57.9 | -68.6 | -37.7 | -50.2 |
| 700----- | -58.2 | -70.4 | -37.9 | -52.2 |
| 800----- | -58.5 | -72.1 | -38.1 | -54.2 |
| 900----- | -58.8 | -73.8 | -38.4 | -56.2 |
| 1,000----- | -59.2 | -75.4 | -38.7 | -58.2 |
| 1,100----- | -59.6 | -77.0 | -39.0 | -60.2 |
| 1,200----- | -60.0 | -78.6 | -39.2 | -62.1 |
| 1,300----- | -60.3 | -80.1 | -39.5 | -64.0 |
| 1,400----- | -60.8 | -81.6 | -39.8 | -65.8 |
| 1,478 ¹ ----- | | | -40.1 | -67.3 |
| 1,478----- | | | -41.5 | -67.3 |
| 1,500----- | -61.2 | -83.1 | -41.5 | -67.6 |

¹ Transition point of ZrO_2 .

TABLE 9.37—HEATS AND FREE ENERGIES OF THE REACTIONS



| T(° K) | Hf | | Zr | |
|--------------------------|----------------------------|----------------------------|----------------------------|----------------------------|
| | ΔH° (kcal) | ΔF° (kcal) | ΔH° (kcal) | ΔF° (kcal) |
| 298.15..... | -51.4 | -49.2 | -74.5 | -72.2 |
| 400..... | -51.4 | -48.5 | -74.5 | -71.4 |
| 500..... | -51.4 | -47.7 | -74.4 | -70.6 |
| 590 ¹ | -51.3 | -47.0 | ----- | ----- |
| 590..... | -75.3 | -47.0 | ----- | ----- |
| 600..... | -75.3 | -46.6 | -74.3 | -69.8 |
| 604 ² | ----- | ----- | -74.3 | -69.8 |
| 604..... | ----- | ----- | -99.6 | -69.8 |
| 700..... | -74.7 | -41.8 | -99.0 | -65.1 |
| 800..... | -74.1 | -37.2 | -98.3 | -60.3 |
| 900..... | -73.6 | -32.6 | -97.6 | -55.6 |
| 923 ³ | -73.4 | -31.6 | -97.5 | -54.5 |
| 923..... | -77.7 | -31.6 | -101.8 | -54.5 |
| 987 ⁴ | -77.2 | -28.4 | -101.2 | -51.3 |
| 987..... | -56.6 | -28.4 | -80.6 | -51.3 |
| 1,000..... | -56.5 | -28.0 | -80.5 | -50.9 |
| 1,100..... | -55.4 | -25.2 | -79.3 | -48.0 |
| 1,135 ⁵ | ----- | ----- | -78.9 | -47.0 |
| 1,135..... | ----- | ----- | -78.0 | -47.0 |
| 1,200..... | -54.3 | -22.5 | -77.2 | -45.2 |
| 1,300..... | -53.3 | -19.9 | -76.1 | -42.6 |
| 1,375 ⁶ | -52.4 | -18.0 | -75.3 | -40.7 |
| 1,375..... | -114.5 | -18.0 | -137.4 | -40.7 |
| 1,400..... | -114.1 | -16.2 | -137.0 | -38.9 |
| 1,500..... | -112.5 | -9.3 | -135.4 | -32.0 |

¹ Normal sublimation point of $\text{HfCl}_4(\text{c})$.

² Normal sublimation point of $\text{ZrCl}_4(\text{c})$.

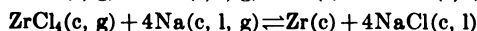
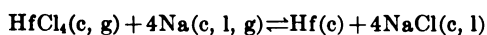
³ Melting point of Mg.

⁴ Melting point of MgCl_2 .

⁵ Transition point of Zr.

⁶ Normal boiling point of Mg.

TABLE 9.38—HEATS AND FREE ENERGIES OF THE REACTIONS



| T(° K) | Hf | | Zr | |
|--------------------------|----------------------------|----------------------------|----------------------------|----------------------------|
| | ΔH° (kcal) | ΔF° (kcal) | ΔH° (kcal) | ΔF° (kcal) |
| 298.15..... | -137.9 | -133.6 | -161.0 | -156.6 |
| 371 ¹ | -138.1 | -132.6 | -161.2 | -155.5 |
| 371..... | -140.6 | -132.6 | -163.7 | -155.5 |
| 400..... | -140.8 | -131.9 | -163.8 | -154.8 |
| 500..... | -141.0 | -129.7 | -164.1 | -152.5 |
| 590 ² | -141.0 | -127.6 | ----- | ----- |
| 590..... | -165.0 | -127.6 | ----- | ----- |
| 600..... | -165.0 | -127.0 | -164.0 | -150.3 |
| 604 ³ | ----- | ----- | -164.0 | -150.2 |
| 604..... | ----- | ----- | -189.3 | -150.2 |
| 700..... | -164.2 | -120.7 | -188.5 | -144.0 |
| 800..... | -163.3 | -114.6 | -187.5 | -137.7 |
| 900..... | -162.2 | -108.6 | -186.3 | -131.5 |
| 1,000..... | -161.0 | -102.6 | -185.0 | -125.5 |
| 1,073 ⁴ | -160.0 | -98.4 | -183.9 | -121.2 |
| 1,073..... | -132.6 | -98.4 | -156.5 | -121.2 |
| 1,100..... | -132.2 | -97.5 | -156.0 | -120.3 |
| 1,135 ⁵ | ----- | ----- | -155.4 | -119.2 |
| 1,135..... | ----- | ----- | -154.5 | -119.2 |
| 1,178 ⁶ | -130.8 | -95.0 | -153.7 | -117.7 |
| 1,178..... | -224.3 | -95.0 | -247.2 | -117.7 |
| 1,200..... | -223.8 | -92.7 | -246.7 | -115.4 |
| 1,300..... | -221.2 | -82.9 | -244.1 | -104.6 |
| 1,400..... | -218.6 | -71.2 | -241.5 | -93.9 |
| 1,500..... | -216.1 | -60.8 | -238.9 | -83.5 |

¹ Melting point of Na.² Normal sublimation point of HfCl₄.³ Normal sublimation point of ZrCl₄.⁴ Melting point of NaCl.⁵ Transition point of Zr.⁶ Normal boiling point of Na.

TABLE 9.39—HEAT CONTENT AND ENTROPY OF $\text{Br}_2(\text{g})$

| T(° K) | $H_T^\circ - H_{298.15}^\circ$ (cal/mole) | S_T° (cal/deg mole) | T(° K) | $H_T^\circ - H_{298.15}^\circ$ (cal/mole) | S_T° (cal/deg mole) |
|-------------|--|-------------------------------|------------|--|-------------------------------|
| 298.15----- | 0 | 58.63 | 1,200----- | 8,050 | 71.00 |
| 400----- | 885 | 61.19 | 1,300----- | 8,955 | 71.72 |
| 500----- | 1,770 | 63.15 | 1,400----- | 9,860 | 72.39 |
| 600----- | 2,655 | 64.77 | 1,500----- | 10,770 | 73.02 |
| 700----- | 3,550 | 66.15 | 1,600----- | 11,675 | 73.61 |
| 800----- | 4,445 | 67.35 | 1,700----- | 12,585 | 74.16 |
| 900----- | 5,345 | 68.40 | 1,800----- | 13,495 | 74.68 |
| 1,000----- | 6,245 | 69.35 | 1,900----- | 14,410 | 75.17 |
| 1,100----- | 7,145 | 70.21 | 2,000----- | 15,325 | 75.64 |

TABLE 9.40—HEAT CONTENT AND ENTROPY OF C (graphite)

| T(° K) | $H_T^\circ - H_{298.15}^\circ$ (cal/mole) | S_T° (cal/deg mole) | T(° K) | $H_T^\circ - H_{298.15}^\circ$ (cal/mole) | S_T° (cal/deg mole) |
|-------------|--|-------------------------------|------------|--|-------------------------------|
| 298.15----- | 0 | 1.36 | 1,200----- | 3,880 | 6.81 |
| 400----- | 250 | 2.08 | 1,300----- | 4,430 | 7.25 |
| 500----- | 570 | 2.79 | 1,400----- | 4,990 | 7.66 |
| 600----- | 950 | 3.48 | 1,500----- | 5,560 | 8.06 |
| 700----- | 1,370 | 4.13 | 1,600----- | 6,150 | 8.44 |
| 800----- | 1,830 | 4.74 | 1,700----- | 6,740 | 8.80 |
| 900----- | 2,320 | 5.31 | 1,800----- | 7,330 | 9.14 |
| 1,000----- | 2,820 | 5.84 | 1,900----- | 7,920 | 9.46 |
| 1,100----- | 3,340 | 6.34 | 2,000----- | 8,530 | 9.77 |

TABLE 9.41—HEAT CONTENT, ENTROPY, HEAT OF FORMATION, AND FREE ENERGY OF FORMATION OF CO(g)

| T(° K) | $H_T^\circ - H_{298.15}^\circ$ (cal/mole) | S_T° (cal/deg mole) | $\Delta H^\circ(f)$ (kcal/mole) | $\Delta F^\circ(f)$ (kcal/mole) |
|-------------|--|-------------------------------|------------------------------------|------------------------------------|
| 298.15..... | 0 | 47.31 | -26.42 | -32.81 |
| 400..... | 710 | 49.35 | -26.32 | -35.01 |
| 500..... | 1,415 | 50.94 | -26.30 | -37.19 |
| 600..... | 2,135 | 52.25 | -26.33 | -39.36 |
| 700..... | 2,875 | 53.38 | -26.41 | -41.53 |
| 800..... | 3,625 | 54.39 | -26.51 | -43.68 |
| 900..... | 4,400 | 55.30 | -26.64 | -45.82 |
| 1,000..... | 5,185 | 56.13 | -26.77 | -47.94 |
| 1,100..... | 5,985 | 56.89 | -26.91 | -50.05 |
| 1,200..... | 6,795 | 57.59 | -27.06 | -52.15 |
| 1,300..... | 7,620 | 58.25 | -27.21 | -54.24 |
| 1,400..... | 8,450 | 58.87 | -27.38 | -56.31 |
| 1,500..... | 9,285 | 59.45 | -27.55 | -58.37 |
| 1,600..... | 10,130 | 59.99 | -27.73 | -60.42 |
| 1,700..... | 10,980 | 60.51 | -27.91 | -62.46 |
| 1,800..... | 11,835 | 61.00 | -28.08 | -64.48 |
| 1,900..... | 12,700 | 61.46 | -28.26 | -66.50 |
| 2,000..... | 13,565 | 61.91 | -28.46 | -68.52 |

TABLE 9.42—HEAT CONTENT, ENTROPY, HEAT OF FORMATION, AND FREE ENERGY OF FORMATION OF $\text{CO}_2(\text{g})$

| T(° K) | $H_T^\circ - H_{298.15}^\circ$ (cal/mole) | S_T° (cal/deg mole) | $\Delta H^\circ(\text{f})$ (kcal/mole) | $\Delta F^\circ(\text{f})$ (kcal/mole) |
|-------------|--|-------------------------------|---|---|
| 298.15----- | 0 | 51.05 | -94.05 | -94.26 |
| 400----- | 955 | 53.80 | -94.07 | -94.32 |
| 500----- | 1,985 | 56.10 | -94.09 | -94.38 |
| 600----- | 3,085 | 58.10 | -94.13 | -94.44 |
| 700----- | 4,255 | 59.88 | -94.17 | -94.49 |
| 800----- | 5,450 | 61.49 | -94.22 | -94.53 |
| 900----- | 6,700 | 62.97 | -94.27 | -94.57 |
| 1,000----- | 7,985 | 64.32 | -94.32 | -94.60 |
| 1,100----- | 9,295 | 65.57 | -94.36 | -94.62 |
| 1,200----- | 10,630 | 66.73 | -94.42 | -94.64 |
| 1,300----- | 11,985 | 67.81 | -94.47 | -94.64 |
| 1,400----- | 13,360 | 68.83 | -94.52 | -94.65 |
| 1,500----- | 14,750 | 69.79 | -94.57 | -94.66 |
| 1,600----- | 16,150 | 70.69 | -94.64 | -94.67 |
| 1,700----- | 17,560 | 71.55 | -94.70 | -94.67 |
| 1,800----- | 18,985 | 72.36 | -94.75 | -94.66 |
| 1,900----- | 20,415 | 73.14 | -94.81 | -94.66 |
| 2,000----- | 22,855 | 73.87 | -94.88 | -94.64 |

TABLE 9.43—HEAT CONTENT AND ENTROPY OF $\text{Cl}_2(\text{g})$

| T(° K) | $H_T^\circ - H_{298.15}^\circ$ (cal/mole) | S_T° (cal/deg mole) | T(° K) | $H_T^\circ - H_{298.15}^\circ$ (cal/mole) | S_T° (cal/deg mole) |
|-------------|--|-------------------------------|------------|--|-------------------------------|
| 298.15----- | 0 | 53.31 | 1,200----- | 7,915 | 65.40 |
| 400----- | 845 | 55.74 | 1,300----- | 8,815 | 66.12 |
| 500----- | 1,700 | 57.65 | 1,400----- | 9,720 | 66.79 |
| 600----- | 2,565 | 59.23 | 1,500----- | 10,630 | 67.42 |
| 700----- | 3,445 | 60.59 | 1,600----- | 11,535 | 68.00 |
| 800----- | 4,330 | 61.77 | 1,700----- | 12,445 | 68.55 |
| 900----- | 5,220 | 62.82 | 1,800----- | 13,360 | 69.08 |
| 1,000----- | 6,115 | 63.76 | 1,900----- | 14,270 | 69.57 |
| 1,100----- | 7,015 | 64.61 | 2,000----- | 15,185 | 70.04 |

TABLE 9.44—HEAT CONTENT AND ENTROPY OF $F_2(g)$

| T(° K) | $H_T^\circ - H_{298.15}^\circ$ (cal/mole) | S_T° (cal/deg mole) | T(° K) | $H_T^\circ - H_{298.15}^\circ$ (cal/mole) | S_T° (cal/deg mole) |
|--------------|--|-------------------------------|-------------|--|-------------------------------|
| 298.15 ----- | 0 | 48.56 | 1,200 ----- | 7,680 | 60.18 |
| 400 ----- | 785 | 50.82 | 1,300 ----- | 8,580 | 60.91 |
| 500 ----- | 1,590 | 52.62 | 1,400 ----- | 9,485 | 61.58 |
| 600 ----- | 2,420 | 54.13 | 1,500 ----- | 10,395 | 62.20 |
| 700 ----- | 3,270 | 55.44 | 1,600 ----- | 11,310 | 62.80 |
| 800 ----- | 4,135 | 56.59 | 1,700 ----- | 12,225 | 63.35 |
| 900 ----- | 5,010 | 57.63 | 1,800 ----- | 13,145 | 63.88 |
| 1,000 ----- | 5,890 | 58.56 | 1,900 ----- | 14,065 | 64.37 |
| 1,100 ----- | 6,785 | 59.41 | 2,000 ----- | 14,990 | 64.85 |

TABLE 9.45—HEAT CONTENT AND ENTROPY OF $I_2(g)$

| T(° K) | $H_T^\circ - H_{298.15}^\circ$ (cal/mole) | S_T° (cal/deg mole) | T(° K) | $H_T^\circ - H_{298.15}^\circ$ (cal/mole) | S_T° (cal/deg mole) |
|--------------|--|-------------------------------|-------------|--|-------------------------------|
| 298.15 ----- | 0 | 62.25 | 1,200 ----- | 8,115 | 74.74 |
| 400 ----- | 905 | 64.85 | 1,300 ----- | 9,025 | 75.47 |
| 500 ----- | 1,795 | 66.85 | 1,400 ----- | 9,935 | 76.15 |
| 600 ----- | 2,690 | 68.48 | 1,500 ----- | 10,850 | 76.77 |
| 700 ----- | 3,590 | 69.87 | 1,600 ----- | 11,765 | 77.37 |
| 800 ----- | 4,495 | 71.07 | 1,700 ----- | 12,680 | 77.92 |
| 900 ----- | 5,395 | 72.13 | 1,800 ----- | 13,595 | 78.44 |
| 1,000 ----- | 6,300 | 73.09 | 1,900 ----- | 14,515 | 78.94 |
| 1,100 ----- | 7,205 | 73.95 | 2,000 ----- | 15,435 | 79.41 |

TABLE 9.46—HEAT CONTENT AND ENTROPY OF $Mg(c, 1, g)$

| T(° K) | $H_T^\circ - H_{298.15}^\circ$ (cal/mole) | S_T° (cal/deg mole) | T(° K) | $H_T^\circ - H_{298.15}^\circ$ (cal/mole) | S_T° (cal/deg mole) |
|------------------------|--|-------------------------------|--------------------------|--|-------------------------------|
| 298.15 ----- | 0 | 7.78 | 1,200 ----- | 8,440 | 19.54 |
| 400 ----- | 615 | 9.55 | 1,300 ----- | 9,180 | 20.13 |
| 500 ----- | 1,255 | 10.98 | 1,375 ² ----- | 9,740 | 20.55 |
| 600 ----- | 1,920 | 12.19 | 1,375 ----- | 40,760 | 43.11 |
| 700 ----- | 2,615 | 13.26 | 1,400 ----- | 40,880 | 43.20 |
| 800 ----- | 3,330 | 14.22 | 1,500 ----- | 41,380 | 43.54 |
| 900 ----- | 4,060 | 15.07 | 1,600 ----- | 41,880 | 43.86 |
| 923 ¹ ----- | 4,230 | 15.26 | 1,700 ----- | 42,380 | 44.17 |
| 923 ----- | 6,390 | 17.60 | 1,800 ----- | 42,880 | 44.45 |
| 1,000 ----- | 6,960 | 18.19 | 1,900 ----- | 43,380 | 44.72 |
| 1,100 ----- | 7,700 | 18.90 | 2,000 ----- | 43,880 | 44.98 |

¹ Melting point.² Normal boiling point.

TABLE 9.47—HEAT CONTENT, ENTROPY, HEAT OF FORMATION, AND FREE ENERGY OF FORMATION $\text{MgCl}_2(\text{c}, 1)$

| T(° K) | $H_T^\circ - H_{298.15}^\circ$ (cal/mole) | S_T° (cal/deg mole) | $\Delta H^\circ(\eta)$ (kcal/mole) | $\Delta F^\circ(\eta)$ (kcal/mole) |
|--------------------------|--|-------------------------------|---------------------------------------|---------------------------------------|
| 298.15----- | 0 | 21.40 | -153.2 | -141.4 |
| 400----- | 1,800 | 26.59 | -152.9 | -137.4 |
| 500----- | 3,650 | 30.71 | -152.5 | -133.55 |
| 600----- | 5,555 | 34.19 | -152.15 | -129.8 |
| 700----- | 7,480 | 37.15 | -151.8 | -126.1 |
| 800----- | 9,420 | 39.74 | -151.45 | -122.45 |
| 900----- | 11,380 | 42.05 | -151.1 | -118.85 |
| 923 ¹ ----- | 11,850 | 42.55 | -151.05 | -118.05 |
| 923----- | 11,850 | 42.55 | -153.2 | -118.05 |
| 987 ² ----- | 13,160 | 43.94 | -152.95 | -115.65 |
| 987----- | 23,460 | 54.38 | -142.6 | -115.65 |
| 1,000----- | 23,750 | 54.67 | -142.55 | -115.25 |
| 1,100----- | 25,960 | 56.78 | -141.95 | -112.55 |
| 1,200----- | 28,170 | 58.70 | -141.4 | -109.9 |
| 1,300----- | 30,380 | 60.47 | -140.85 | -107.35 |
| 1,375 ³ ----- | 32,040 | 61.69 | -140.4 | -105.4 |
| 1,375----- | 32,040 | 61.69 | -171.45 | -105.4 |
| 1,400----- | 32,590 | 62.10 | -171.25 | -104.2 |
| 1,500----- | 34,800 | 63.63 | -170.45 | -99.45 |
| 1,600----- | 37,010 | 65.06 | -169.65 | -94.75 |
| 1,700----- | 39,220 | 66.40 | -168.8 | -90.1 |
| 1,800----- | 41,430 | 67.66 | -168.05 | -85.45 |
| 1,900----- | 43,640 | 68.85 | -167.25 | -80.9 |
| 2,000----- | 45,850 | 69.99 | -166.45 | -76.4 |

¹ Melting point of Mg.² Melting point of MgCl_2 .³ Normal boiling point of Mg.TABLE 9.48—HEAT CONTENT AND ENTROPY OF $\text{N}_2(\text{g})$

| T(° K) | $H_T^\circ - H_{298.15}^\circ$ (cal/mole) | S_T° (cal/deg mole) | T(° K) | $H_T^\circ - H_{298.15}^\circ$ (cal/mole) | S_T° (cal/deg mole) |
|-------------|--|-------------------------------|------------|--|-------------------------------|
| 298.15----- | 0 | 45.77 | 1,200----- | 6,720 | 55.96 |
| 400----- | 710 | 47.82 | 1,300----- | 7,530 | 56.61 |
| 500----- | 1,415 | 49.39 | 1,400----- | 8,355 | 57.22 |
| 600----- | 2,125 | 50.69 | 1,500----- | 9,180 | 57.79 |
| 700----- | 2,855 | 51.81 | 1,600----- | 10,020 | 58.33 |
| 800----- | 3,595 | 52.80 | 1,700----- | 10,860 | 58.84 |
| 900----- | 4,355 | 53.69 | 1,800----- | 11,710 | 59.33 |
| 1,000----- | 5,130 | 54.51 | 1,900----- | 12,565 | 59.79 |
| 1,100----- | 5,920 | 55.26 | 2,000----- | 13,425 | 60.23 |

TABLE 9.49—HEAT CONTENT AND ENTROPY OF O₂(g)

| T(°K) | $H_T^\circ - H_{298.15}^\circ$ (cal/mole) | S_T° (cal/deg mole) | T(°K) | $H_T^\circ - H_{298.15}^\circ$ (cal/mole) | S_T° (cal/deg mole) |
|-------------|--|-------------------------------|------------|--|-------------------------------|
| 298.15----- | 0 | 49.01 | 1,200----- | 7,115 | 59.74 |
| 400----- | 725 | 51.10 | 1,300----- | 7,970 | 60.43 |
| 500----- | 1,455 | 52.73 | 1,400----- | 8,835 | 61.07 |
| 600----- | 2,210 | 54.11 | 1,500----- | 9,705 | 61.67 |
| 700----- | 2,980 | 55.30 | 1,600----- | 10,585 | 62.23 |
| 800----- | 3,785 | 56.37 | 1,700----- | 11,465 | 62.77 |
| 900----- | 4,600 | 57.33 | 1,800----- | 12,355 | 63.27 |
| 1,000----- | 5,425 | 58.20 | 1,900----- | 13,250 | 63.76 |
| 1,100----- | 6,265 | 59.00 | 2,000----- | 14,150 | 64.22 |

TABLE 9.50—HEAT CONTENT AND ENTROPY OF Na(c, l, g)

| T(°K) | $H_T^\circ - H_{298.15}^\circ$ (cal/mole) | S_T° (cal/deg mole) | T(°K) | $H_T^\circ - H_{298.15}^\circ$ (cal/mole) | S_T° (cal/deg mole) |
|------------------------|--|-------------------------------|--------------------------|--|-------------------------------|
| 298.15----- | 0 | 12.23 | 1,178 ² ----- | 6,840 | 23.70 |
| 350----- | 360 | 13.34 | 1,178----- | 30,220 | 43.55 |
| 371 ¹ ----- | 514 | 13.77 | 1,200----- | 30,330 | 43.64 |
| 371----- | 1,136 | 15.44 | 1,300----- | 30,825 | 44.03 |
| 400----- | 1,355 | 16.01 | 1,400----- | 31,325 | 44.41 |
| 500----- | 2,095 | 17.67 | 1,500----- | 31,820 | 44.75 |
| 600----- | 2,820 | 18.99 | 1,600----- | 32,315 | 45.07 |
| 700----- | 3,520 | 20.07 | 1,700----- | 32,815 | 45.37 |
| 800----- | 4,220 | 21.00 | 1,800----- | 33,310 | 45.65 |
| 900----- | 4,910 | 21.81 | 1,900----- | 33,805 | 45.92 |
| 1,000----- | 5,595 | 22.54 | 2,000----- | 34,305 | 46.17 |
| 1,100----- | 6,295 | 23.21 | | | |

¹ Melting point.² Normal boiling point.

TABLE 9.51—HEAT CONTENT, ENTROPY, HEAT OF FORMATION, AND FREE ENERGY OF FORMATION OF NaCl (c, l)

| T(° K) | $H_T^\circ - H_{298.15}^\circ$ (cal/mole) | S_T° (cal/deg mole) | $\Delta H^\circ(f)$ (kcal/mole) | $\Delta F^\circ(f)$ (kcal/mole) |
|--------------------------|--|-------------------------------|------------------------------------|------------------------------------|
| 298.15..... | 0 | 17.30 | -98.25 | -91.8 |
| 350..... | 630 | 19.12 | -98.15 | -90.65 |
| 371 ¹ | 885 | 19.86 | -98.15 | -90.2 |
| 371..... | 885 | 19.86 | -98.8 | -90.2 |
| 400..... | 1,240 | 20.88 | -98.75 | -89.55 |
| 500..... | 2,510 | 23.71 | -98.65 | -87.25 |
| 600..... | 3,830 | 26.12 | -98.5 | -85.0 |
| 700..... | 5,190 | 28.21 | -98.3 | -82.8 |
| 800..... | 6,590 | 30.08 | -98.05 | -80.6 |
| 900..... | 8,020 | 31.76 | -97.75 | -78.4 |
| 1,000..... | 9,480 | 33.30 | -97.4 | -76.3 |
| 1,073 ² | 10,580 | 34.36 | -97.15 | -74.75 |
| 1,073..... | 17,430 | 40.74 | -90.3 | -74.75 |
| 1,100..... | 17,860 | 41.14 | -90.15 | -74.35 |
| 1,178 ³ | 19,110 | 42.23 | -89.8 | -73.25 |
| 1,178..... | 19,110 | 42.23 | -113.2 | -73.25 |
| 1,200..... | 19,460 | 42.54 | -113.05 | -72.5 |
| 1,300..... | 21,060 | 43.82 | -112.4 | -69.15 |
| 1,400..... | 22,660 | 45.00 | -111.75 | -65.85 |
| 1,500..... | 24,260 | 46.11 | -111.1 | -62.6 |
| 1,600..... | 25,860 | 47.14 | -110.45 | -59.35 |
| 1,700..... | 27,460 | 48.11 | -109.8 | -56.2 |
| 1,800..... | 29,060 | 49.02 | -109.15 | -53.05 |
| 1,900..... | 30,660 | 49.89 | -108.5 | -49.95 |
| 2,000..... | 32,260 | 50.71 | -107.85 | -46.9 |

¹ Melting point of Na.² Melting point of NaCl.³ Normal boiling point of Na.

TABLE 9.52—HEAT CONTENT AND ENTROPY OF Zr (α , β)

| T(° K) | $H_T^\circ - H_{298.15}^\circ$ (cal/mole) | S_T° (cal/deg mole) | T(° K) | $H_T^\circ - H_{298.15}^\circ$ (cal/mole) | S_T° (cal/deg mole) |
|--------------------------|--|-------------------------------|------------|--|-------------------------------|
| 298.15----- | 0 | 9.29 | 1,135----- | 7,090 | 19.71 |
| 400----- | 665 | 11.20 | 1,200----- | 7,560 | 20.11 |
| 500----- | 1,350 | 12.73 | 1,300----- | 8,290 | 20.69 |
| 600----- | 2,065 | 14.03 | 1,400----- | 9,015 | 21.23 |
| 700----- | 2,800 | 15.17 | 1,500----- | 9,740 | 21.73 |
| 800----- | 3,550 | 16.17 | 1,600----- | 10,470 | 22.20 |
| 900----- | 4,315 | 17.07 | 1,700----- | 11,200 | 22.65 |
| 1,000----- | 5,095 | 17.89 | 1,800----- | 11,920 | 23.06 |
| 1,100----- | 5,890 | 18.65 | 1,900----- | 12,650 | 23.45 |
| 1,135 ¹ ----- | 6,170 | 18.90 | 2,000----- | 13,380 | 23.83 |

¹ Transition point.TABLE 9.53—HEAT CONTENT, ENTROPY, HEAT OF FORMATION, AND FREE ENERGY OF FORMATION OF ZrO₂ (α , β)

| T(° K) | $H_T^\circ - H_{298.15}^\circ$ (cal/mole) | S_T° (cal/deg mole) | $\Delta H^\circ(\eta)$ (kcal/mole) | $\Delta F^\circ(\eta)$ (kcal/mole) |
|--------------------------|--|-------------------------------|---------------------------------------|---------------------------------------|
| 298.15----- | 0 | 12.12 | -261.5 | -247.7 |
| 400----- | 1,475 | 16.36 | -261.4 | -243.0 |
| 500----- | 3,050 | 19.87 | -261.3 | -238.5 |
| 600----- | 4,690 | 22.86 | -261.1 | -233.9 |
| 700----- | 6,380 | 25.46 | -260.9 | -229.4 |
| 800----- | 8,120 | 27.80 | -260.7 | -224.9 |
| 900----- | 9,910 | 29.91 | -260.5 | -220.5 |
| 1,000----- | 11,730 | 31.82 | -260.3 | -216.0 |
| 1,100----- | 13,570 | 33.58 | -260.1 | -211.6 |
| 1,135 ¹ ----- | 14,220 | 34.14 | -260.0 | -210.1 |
| 1,135----- | 14,220 | 34.14 | -260.9 | -210.1 |
| 1,200----- | 15,420 | 35.19 | -260.7 | -207.2 |
| 1,300----- | 17,280 | 36.67 | -260.5 | -202.7 |
| 1,400----- | 19,150 | 38.06 | -260.2 | -198.3 |
| 1,478 ² ----- | 20,620 | 39.08 | -260.0 | -194.8 |
| 1,478----- | 22,040 | 40.04 | -258.6 | -194.8 |
| 1,500----- | 22,430 | 40.30 | -258.5 | -193.9 |
| 1,600----- | 24,210 | 41.45 | -258.3 | -189.6 |
| 1,700----- | 25,990 | 42.53 | -258.2 | -185.3 |
| 1,800----- | 27,770 | 43.55 | -258.0 | -181.0 |
| 1,900----- | 29,550 | 44.51 | -257.8 | -176.7 |
| 2,000----- | 31,330 | 45.42 | -257.7 | -172.4 |

¹ Transition point of Zr.² Transition point of ZrO₂.

TABLE 9.54—HEAT CONTENT, ENTROPY, HEAT OF FORMATION, AND FREE ENERGY OF FORMATION OF $\text{ZrCl}_4(\text{c})$

| T(° K) | $H_T^\circ - H_{298.15}^\circ$ (cal/mole) | S_T° (cal/deg mole) | $\Delta H^\circ(\text{f})$ (kcal/mole) | $\Delta F^\circ(\text{f})$ (kcal/mole) |
|------------------------|--|-------------------------------|---|---|
| 298.15..... | 0 | 44.50 | -231.9 | -210.6 |
| 400..... | 3,005 | 53.15 | -231.2 | -203.4 |
| 500..... | 6,050 | 59.94 | -230.6 | -196.6 |
| 600..... | 9,120 | 65.54 | -230.0 | -189.8 |
| 604 ¹ | 9,240 | 65.75 | -230.0 | -189.6 |
| 700..... | 12,220 | 70.31 | -229.4 | -183.1 |

¹ Normal sublimation point.TABLE 9.55—HEAT CONTENT, ENTROPY, HEAT OF FORMATION, AND FREE ENERGY OF FORMATION OF $\text{ZrCl}_4(\text{c})$

| T(° K) | $H_T^\circ - H_{298.15}^\circ$ (cal/mole) | S_T° (cal/deg mole) | $\Delta H^\circ(\text{f})$ (kcal/mole) | $\Delta F^\circ(\text{f})$ (kcal/mole) |
|--------------------------|--|-------------------------------|---|---|
| 298.15..... | 0 | 90.48 | -204.9 | -197.3 |
| 400..... | 2,440 | 97.51 | -204.8 | -194.7 |
| 500..... | 4,900 | 103.00 | -204.7 | -192.1 |
| 600..... | 7,400 | 107.56 | -204.7 | -189.6 |
| 604 ¹ | 7,500 | 107.72 | -204.7 | -189.6 |
| 700..... | 9,920 | 111.44 | -204.6 | -187.1 |
| 800..... | 12,460 | 114.83 | -204.6 | -184.6 |
| 900..... | 15,010 | 117.84 | -204.6 | -182.1 |
| 1,000..... | 17,560 | 120.52 | -204.6 | -179.6 |
| 1,100..... | 20,120 | 122.96 | -204.7 | -177.1 |
| 1,135 ² | 21,020 | 123.77 | -204.7 | -176.2 |
| 1,135..... | 21,020 | 123.77 | -205.6 | -176.2 |
| 1,200..... | 22,680 | 125.19 | -205.6 | -174.6 |
| 1,300..... | 25,250 | 127.25 | -205.5 | -172.0 |
| 1,400..... | 27,820 | 129.15 | -205.5 | -169.4 |
| 1,500..... | 30,390 | 130.92 | -205.5 | -166.9 |

¹ Normal sublimation point of $\text{ZrCl}_4(\text{c})$.² Transition point of Zr.

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Appendix A

ENGINEERING DATA SHEETS—ARC-MELTED IODIDE HAFNIUM

Typical Analysis (ppm)

| | | | | | |
|----|-----|----|-----|----|-------|
| Al | 50 | H | <30 | N | 20 |
| B | <5 | Fe | 100 | O | 500 |
| Cd | <1 | Pb | <10 | Si | <10 |
| C | 50 | Mg | <10 | Sn | <10 |
| Cr | <10 | Mn | <10 | Ti | <10 |
| Co | <10 | Mo | <10 | W | <50 |
| Cu | 50 | Ni | <10 | Zr | 2.25% |

Processing

1. Fabricating Conditions:

Forging Temperature 2,000° F (1,095° C)

Rolling Temperature 1,700° F (930° C)

Extrusion Temperature 2,000° F (1,095° C)

2. Annealing: Recrystallization occurs in the range 1,475–1,650° F (800–900° C), 1 hour

3. Fusion Welding With Tungsten Electrode for ¼-Inch Thick Plate,
Butt Welds:

220 amps

16 volts

6¼ in./min

Physical Properties

1. Transformation Temperature: 3,200° F (1,760° C)

Melting Point: 4,032° F (2,222° C)

2. Thermal Expansivity-Alpha-Phase: $5.9 \times 10^{-6}/^{\circ}\text{C}$ (20–200° C)

3. Lattice Parameters:

| | | |
|-------|----------|--------------------------|
| a_0 | 3.1883 Å | } close-packed hexagonal |
| c_0 | 5.0422 Å | |
| a_0 | 3.50 Å | body-centered cubic |

4. Vapor Pressure:
 10^{-10} atm at 1,867° C (3,032° F)
 10^{-9} atm at 2,007° C (3,645° F)
5. Electrical Properties:
 Resistivity (25° C) 35.1 μ ohm-cm
 Temperature coefficient $38 \times 10^{-4}/^\circ\text{C}^\circ$
6. Elastic Properties:
 Young's Modulus 19.8×10^6 psi (70° F)
7. Thermal Conductivity (at 50° C):
 0.223 watts/cm- $^\circ\text{C}^\circ$
8. Magnetic Properties:
 Paramagnetic susceptibility 0.42×10^{-6} emu/g (20° C)
 Hall Coefficient 0.162×10^{-13} volt cm/amp gauss
9. Density: 13.09 g/cc
10. Thermal neutron absorption cross section: 105 barns

Mechanical Properties

1. Tensile Properties (Longitudinal Direction):

| Temperature (° F) | Strength (psi) | | Elongation in 2 in. (%) | R.A. (%) |
|-------------------|----------------|---------|----------------------------|----------|
| | Yield (0.2%) | Tensile | | |
| Room..... | 33, 600 | 64, 800 | 23 | 37 |
| 300..... | 28, 700 | 53, 200 | 29 | 44 |
| 500..... | 22, 300 | 42, 000 | 36 | 46 |
| 700..... | 15, 700 | 33, 700 | 43 | 57 |

Material annealed 15 minutes at 1,700° F (926° C)

2. Impact Properties (Subsize Izod—V-Notch):
 2.7 ft-lb at room temperature
3. Creep Properties (Longitudinal):
 Stress for minimum creep rate of 10^{-6} /hr at 500–700° F (260–370° C) in approximately 23,000 psi.
4. Fatigue Properties (Longitudinal):

| Temperature (° F) | Fatigue strength at 2×10^7 cycles (psi) | | Endurance ratio |
|-------------------|---|-----------|--------------------|
| | Notched | Unnotched | |
| RT..... | 19, 500 | 27, 500 | 0. 50 |
| 700..... | 12, 500 | 17, 500 | 0. 65 |

High temperature water corrosion resistance

| Water temperature (° F) | Weight gain after 195 days (mg/dm ²) |
|-------------------------|---|
| 600..... | 6 |
| 680..... | 7-9 |
| 750 (steam)..... | 7 |

Appendix B

INDUSTRIAL HYGIENE AND SAFETY

By E. C. BARNES ¹

Introduction

The major factor to be considered in the safe use of hafnium is its exothermic reaction with a number of other elements and compounds. Bars, ingots, and other substantial pieces of the metal can be heated to high temperatures without burning. Fine dusts, however, will explode when dispersed in air. Thin turnings or chips are easily ignited and burn with extremely high temperatures. The physical state of the metal is, therefore, extremely important in evaluating possible hazards. The greater the ratio of surface to mass, the greater the fire or explosion hazard. A possible indirect hazard produced by reactions of hafnium with other elements must be also considered, such as an explosion hazard due to release and combustion of hydrogen when hafnium reacts with water. The metal itself has a low order of toxicity, and no serious limitations are necessary for control of health hazards, unless the metal is either chemically combined or alloyed with other materials having higher degrees of toxicity.

The availability of data needed to evaluate accurately those properties and reactions of hafnium which are possible hazards in its use is extremely limited. In general, it appears that hafnium sponge may be more sensitive to ignition in air than zirconium sponge. The amount of impurities, particularly iron, has a marked influence on this characteristic. As the amount of impurities increases, the sensitivity goes up. Hafnium turnings or chips appear to have characteristics similar to zirconium. The data on zirconium [1] can be used as a guide until adequate data are available on hafnium.

Explosion and Fire Hazard

Dust clouds of hafnium powder will explode if there is a source of ignition and if the concentration exceeds the lower explosive limit. If the particle size in an air-dust cloud is small enough, the dust will

¹ Westinghouse Atomic Power Division.

frequently ignite and explode. There are no data to indicate the exact limits of the conditions necessary for self-ignition. This would vary with mean particle size, size distribution, temperature, humidity, and surface characteristics of the particles. Dust with a mean particle size below 15 to 20 microns should be considered as being in the size range which will exhibit this self-ignition characteristic.

Inert gases such as helium or argon are used to prevent ignition of powders or sponge. Carbon dioxide and nitrogen should not be used for this purpose, since they have been shown to be ineffective in preventing the explosion of dust clouds of metals such as zirconium.

From these considerations it becomes apparent that extreme care must be taken in any situation involving the use of fine hafnium powder. Dust clouds are very easily ignited and produce relatively high explosion pressures. Layers of such dust will also easily ignite and burn with a high temperature even though they are not dispersed as a cloud in the air. The burning of such dust in a closed vessel will result in a rapid pressure rise because of the expansion of air or other gas in the vessel.

Hafnium powder wet with water is much safer to handle than the dry powder because it is more difficult to ignite. Once ignited, however, the wet powder will burn even more violently than dry powder, partly because the metal will decompose the water and use the oxygen for its own combustion and partly because the steam formed within the burning mass will scatter the metal. Small percentages of water in the powder would be the most dangerous.

In general, it is good practice to handle the hafnium powder in very small batches (a few ounces) if the material is dry. Otherwise, good control of the explosion risk must be expertly maintained. Sources of ignition such as heat, flame, friction, and sparks should be avoided. Situations which might result in the dispersion of a cloud of dust in air or other gases, such as nitrogen and carbon dioxide, which may react with the hafnium should be avoided. Since helium and argon will not react with hafnium dust, they can be used to provide an inert atmosphere.

Definite procedures for disposal of fine powders must be established and rigidly followed. Although it is not practical to specify all details of disposal because of the many different factors which might be involved, controlled burning of such powders is the disposal method generally preferred. Considerable care must be taken that all the hafnium powder is completely burned to avoid the possibility of subsequent fires or explosions. The resulting oxide is inert and can be handled without special precaution.

All waste, rags, containers, etc., which have been in contact with hafnium powder should be put into separate waste cans filled with

water containing a good wetting agent, and the cans should be delivered at scheduled intervals to the incinerator. The fireman should be instructed to burn these hafnium wastes in a hot fire immediately after they are received. They should be fired in small quantities to avoid the possibility of a large flareback. The risk can be reduced by processing, handling, or storing such materials in small quantities. Any storage of waste should be in a fireproof enclosure constructed in such a manner that a fire would not involve surrounding areas or buildings. Outdoor storage may be satisfactory if containers are used which prevent entrance of ignition sources, such as sparks.

Hafnium sponge and turnings, chips, or dust from the metal can be rather easily ignited and will burn with an extremely high temperature. Very little flame results, but the metal gives an incandescent glow while it is burning. Turnings or chips from machine operations may start to burn if the machining operation produces sufficiently high temperature in the turnings or chips. They will also ignite easily from sparks or small flames. Once the burning has started, it is very difficult to stop. The heat from a hafnium waste fire of sufficient size can distort a machine-tool bed and burn holes through sheet metal. If the sponge has been treated so that all oxide film is removed, such as in the iodide process of producing crystal bar, contact with air will initiate burning.

From these properties of turnings, chips, and sponge it becomes apparent that certain precautions must be taken to minimize the fire hazard. Where processes produce an "activated" surface, steps must be taken which will inactivate the surface before it comes in contact with air. Flooding masses of activated sponge with a large volume of water prior to any contact with air will result in a de-activation of the surface that permits handling with decreased risk. In one instance, water dumped within a few seconds into a container holding several hundred pounds of "activated" sponge sufficiently de-activated the surface so that the sponge could be exposed to air without self-igniting. Speed in adding the water is very important. If the sponge is kept wet, it will not self-ignite. If the sponge is stored in water for a considerable length of time, there may be a small evolution of hydrogen, and protection must be provided against the ignition of the hydrogen.

The coolant used during machining operations is usually a cutting oil or a water-oil emulsion, although an air jet has been used successfully. These coolants conduct the heat away from the turnings and chips with sufficient rapidity to prevent ignition. The rate of flow of the coolant must be kept high, and there must be continual observation to prevent any stoppage of the flow. Complete immersion of the surface being machined has been practical in some cases. Only small amounts of turnings or chips should be allowed to collect

on a machine before removal. If these are removed in small batches and placed in covered metal cans, the risk of a damaging fire is reduced. If small amounts start to burn, they can be allowed to burn out without damage to the machines. If, for any reason, it is not possible to use coolants on machines cutting hafnium, sharp tools and extremely slow feeds and cutting speeds must be used to prevent the generation of enough heat to ignite the turnings or chips. (Small chips or turnings are more easily ignited.)

A variance in ignition characteristics of hafnium sponge has been noted. Some batches or grades of material seem to ignite more easily than others. This characteristic is not fully understood but must be taken into account when planning for proper protection. Contamination by iron tends to increase the metal's pyrophoric tendency.

If turnings or chips have no salvage value, they can be burned in small quantities at a safe location merely by lighting with a small flame. Such burning should be done outside of buildings and at a location where there are no other flammable materials.

If hafnium wastes are stored under water for long periods precautions must be taken to prevent the loss of water from the storage containers by leakage, evaporation, etc.

Wet-collection methods should be used for hafnium dust. The system should be carefully designed with short ducts between hood and dust collector so that there will be no accumulation of materials that might ignite and burn.

The National Fire Code [2] does not cover hafnium powder or dust. However, many suggestions which can be applied to hafnium are included in the section on magnesium powder or dust.

Fire Control

When quantities of turnings are kept to a minimum, a small fire can be put out with a bucket of water or it can be smothered with several scoops of graphite powder or the commercially available G-1 or Metal-X powders. Small quantities of water should never be applied to burning hafnium, but large volumes of water can be applied successfully when conditions are such that the water can quickly cover the heated hafnium.

Fire extinguishers equipped with G-1 or Metal-X powders only should be used on hafnium fires. Since the powders are intended to smother the fire, they must be applied carefully in order to avoid dispersing the burning material over a larger area. Common fire-extinguishing agents, such as carbon dioxide, foam, and carbon tetrachloride, should never be used on a hafnium fire. They will merely increase the rate of burning. Water, or other fire-extinguish-

ing agents, can be used to control fires of wood or other flammables which may become ignited in the vicinity of the hafnium fire. Within a closed container, fires can also be extinguished with helium or argon in sufficient quantity. The conditions must be such that air is completely excluded, and the mass must be allowed to cool to room temperature before air is admitted.

Shipment

The Interstate Commerce Commission Regulations [3] must be followed when shipping hafnium. The Regulations in effect March 19, 1958, do not require any special packaging or handling for bars, ingots, sheets, or any other form larger than 20 mesh. There are no special requirements for wet sponge. The containers for wet sponge must, of course, retain the water to prevent any drying out of the sponge since shipping dry sponge involves special requirements.

The ICC Regulations for hafnium metal powder, wet or sludge, permit shipments of 10 lbs or less by metal can and 50 lbs or less by drums. Both must be enclosed in wooden boxes. Wooden kegs, not to exceed 75 lbs net, are permitted. Shipment of dry hafnium metal powder is limited to 10 lbs in a metal container inside a wooden box or 1 lb in a glass or metal container inside a fiber box. Hafnium sponge may be shipped in 30-gallon drums.

The above statements are not intended to cover all the requirements of the ICC, but rather to give an indication of the type of materials and the general nature of restrictions imposed. The Regulations should be consulted for complete requirements. Yellow labels of a design specified in the Regulations are required on packages containing flammable solids such as hafnium.

Toxicity

According to the best information available at the time of writing, it appears that hafnium has a low order of toxicity; no occupational case of systemic poisoning in man has so far been reported. Compounds of hafnium and of zirconium have similar characteristics. They are alike not only in physical and chemical properties, but also in LD_{50} values and in effects on isolated tissues [4]. Observations of Kittle, *et al.* [5], indicate that the LD_{50} for hafnium sodium mandelate for a 10-day observation period is approximately 75 to 100 mg hafnium metal per kg, intravenously in rats. A study of the distribution and excretion of hafnium in the rat was reported by MacDonald and Bahner [6]. Because hafnium is normally present with zirconium and because it is difficult to separate them completely, indirect evidence that the toxicity of hafnium is similar

to that of zirconium has probably been developed in studies on the toxicity of zirconium.

Although there is no evidence to suggest any health hazard from the industrial use of hafnium, it is recommended that any case of significant or high exposure to dust or fumes be investigated for possible reaction by appropriate physical examination and the data be reported in the literature.

Miscellaneous

There is a possibility of an explosion hazard from hydrogen that is released when hafnium is in contact with water. At room temperature it is doubtful that there would be any reaction. The reaction, if any, would be very slight and of no concern, unless the materials were so enclosed as to prevent diffusion and make possible the effective retention of hydrogen over a long period of time. At elevated temperatures, or when hafnium is burning, the reaction between water and the metal would be rapid with considerable release of hydrogen.

This generation of hydrogen, which can be released into surrounding spaces, and the attendant explosion hazard, should be given full consideration in water-cooled furnaces or other equipment where considerable quantities of water might come in contact with fairly large masses of hot metal. The amount of hydrogen which could be generated under these conditions might be large, and if it were released into a building or enclosure, a destructive explosion could occur. Such equipment should be designed to conduct any hydrogen which might be generated to a safe location for release.

Experience with zirconium-uranium alloys [7] indicates that goggles, face shields, and protective clothing are essential during pickling or etching of hafnium alloys. Any new process involving new alloys or methods of pickling should first be tested on a small scale to determine whether an explosive coating might form on the surface of the metal. A careful visual inspection should be made, and the specimen should be tested by rubbing or striking it after careful drying. Such a rubbing or striking test should not be considered as conclusive proof that the surface is free of explosive material, since there have been instances in which samples of zirconium-uranium alloy failed to burn when tested, but exploded violently when placed in a nitric acid bath. Such samples should be handled carefully. If any coating is present, it should be removed by immersing the sample in water to which a small amount of hydrofluoric acid has been added.

There have been many instances of explosions from residues, coatings, or activated surfaces on a variety of metals such as Zircaloy-2; uranium [8]; uranium alloyed with niobium, tin, lead, bismuth,

copper, antimony, gold, or zirconium [9]; titanium [10]; titanium-manganese alloy [11]; and thorium [12]. These explosions emphasize the need for careful preliminary testing and for the use of adequate personal protective equipment whenever new processes involving the more pyrophoric metals such as hafnium are being developed. The treatment of these metals in nitric acid or fuming nitric acid should be done with particular caution.

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Appendix C

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Appendix D

GLOSSARY

| | | |
|--------------------------------|---|---|
| Iodide Process..... | } | The process developed by van Arkel and de Boer and used for refining zirconium and hafnium by the decomposition of the iodide on a hot wire. |
| van Arkel-de Boer Process..... | | |
| Crystal Bar Process..... | | |
| Crystal Bar..... | } | Hafnium produced by the van Arkel-de Boer process. |
| Iodide Metal..... | | |
| Sponge..... | | Hafnium produced by the Kroll process. |
| Nonconsumably Melted..... | | Arc melting in a water-cooled crucible using a tungsten electrode. |
| Consumably Melted..... | | Arc melting in a water-cooled crucible using an electrode made of the material to be melted. |
| Zircaloy-2..... | | An alloy of sponge zirconium with 1.2-1.7 w/o Sn, 0.07 to 0.20% Fe, 0.05 to 0.15 w/o Cr, and 0.03 to 0.08% Ni. |
| Electron Beam Melting..... | | Melting process in which heat is supplied by a beam of electrons directed at the metal in high vacuum. |
| Control Rod..... | | A rod, usually cruciform or "Y" shaped, which is inserted or withdrawn from the core of a nuclear reactor for the purpose of controlling power level. |

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